# **National Ambient Air Monitoring Strategy**



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#### **Section 1 Introduction and Overview**

## 1.1 Background

Monitoring data are a critical part of the Nation's air program infrastructure. In general, the Nation's ambient air monitoring networks:

- inform the public of air quality levels and exposure;
- establish the compliance status of cities and other areas;
- track air quality trends and evaluate progress of emission control programs;
- support development of emission control and air quality research programs.

Monitoring programs, which are operated largely by State and local agencies and Tribal (SLT)Nations, are subject to continual changes in local, State, tribal, Federal and academic priorities. New and revised national ambient air quality standards (NAAQS) and other regulatory needs, changing air quality (e.g., general trend toward reduced concentrations of criteria pollutants), and an influx of scientific findings and technological advancements challenge the response capability of the Nation's networks. The single pollutant measuring approach commonly administered in networks is not an optimal design for recent integrated air quality management trends such as the linkages across ozone, fine particulate matter, regional haze, air toxics, and multi-media interactions (e.g., atmospheric deposition). Indeed, the current design of the Nation's networks still is based largely on the existing monitoring regulations (Code of Federal Regulations, parts 53 and 58) that were developed in the late 1970's.

The United States spends well over \$200 million annually on routine ambient air monitoring programs. These include a variety of different networks (see more detailed discussion and maps in **Attachment 1.1**), with differing objectives:

## (1) <u>State and Local Air Monitoring Stations (SLAMS) and National Air</u> Monitoring Stations (NAMS).

SLAMS and NAMS represent the majority of all criteria pollutant (SO<sub>2</sub>, NO<sub>2</sub>, CO, O<sub>3</sub>, Pb, PM<sub>2.5</sub>, PM<sub>10</sub>) monitoring across the Nation with over 5000 monitors at approximately 3000 sites. These stations use Federal Reference or Equivalent methods (FRM/FEM) for direct comparison to the NAAQS. Design and measurement requirements for these networks are codified in the Code of Federal Regulations (CFR) parts 58 (design and quality assurance), 53 (equivalent methods) and 50 (reference methods). NAMS are a subset of SLAMS that are designated as national trends sites. The NAMS and SLAMS were developed in the 1970's with a major addition of PM<sub>2.5</sub> monitors starting in 1999 associated with promulgation of the 1997 PM NAAQS. These networks experienced accelerated growth throughout the 1970s with most components exhibiting declines in the number of sites with the exception of ozone and PM<sub>2.5</sub>.

## (2) PM<sub>2.5</sub> Networks

The PM<sub>2.5</sub> networks includes three major components:

- a.) **mass only measurements** through nearly 1100 FRM filter-based mass sites that measure 24 hour averaged concentrations through gravimetry, and approximately 200 continuously operating mass sites using a range of technologies;
- b) **chemical speciation measurements** that consists of approximately 50 trend, 250 State Implementation Plan (SIP) and 150 IMPROVE sites, respectively. The vast majority of these sites collect aerosol samples over 24 hours every third day on filters that are analyzed for trace elements, major ions (sulfates, nitrates and ammonium) and organic and elemental carbon fractions. Most of the IMPROVE sites are operated by personnel from the Federal Land Management (FLM) and Forest and National Park Services; and
- c) **research "supersites"** executed as cooperative agreements with Universities and EPA that operate over various periods spanning 1999 to 2003 and conduct a wealth of standard and research grade measurements. Supersites are designed to address the extremely complicated sampling issues associated with fine aerosols and constitute an ambitious technology transfer and liaison effort across research level and routine network operations.

#### 3) Clean Air Status and Trends Network (CASTNET)

CASTNET originally was designed to account for progress of strategies targeting major electrical generating utilities throughout the Midwest which release acid rain precursor emissions, sulfur and nitrogen oxides. Network operations are contracted out to private firms funded through Science and Technology (S&T) funds and managed by EPA's Office of Air and Radiation. CASTNET consists of approximately 70 sites located predominantly throughout the East with the greatest site densities in States along the Ohio River Valley and central Appalachian Mountains. Aggregate 2-week samples are collected by filter packs and analyzed for major sulfur and nitrogen oxide transformation compounds (e.g., end products such as sulfate and nitrate ions). CASTNET was deployed in the 1980s as part EPA's National Acid Precipitation Assessment Program (NAPAP). A network assessment in the mid-1990's led to a more optimized and less extensive network.

#### 4) Photochemical Assessment Measurement Stations (PAMS).

PAMS measures ozone precursors {volatile organic compounds (VOC) and nitrogen oxides (NOx) } which react to form ozone at 75 sites in 25 metropolitan areas that were classified as serious ozone nonattainment coincident with release

of the 1990 Clean Air Act (CAA) Amendments. The addition of PAMS in the early to mid-1990's was a major addition to the national networks, introducing near research grade measurement technologies to produce continuous data for over 50 VOC compounds during summer ozone seasons. More recently, PAMS has been subject to numerous concerns regarding data quality and lack of data analysis applications. Recent efforts have explored stronger linkage to air toxics monitoring as well as identification of more streamlined PAMS requirements.

## 5) Air Toxics Monitoring Network.

Nearly 250 air toxics sites have been operated by State and local agencies largely through their own initiatives and funding as there are no Federal requirements for air toxics monitoring, and only recently have Federal grant funds been earmarked for toxics monitoring. A steering committee consisting of EPA and State and local agency members has been developing a National Air Toxics monitoring program. The program design effort is starting with a detailed analysis of data from existing sites and recently deployed pilot studies (measuring 18 species) at four major urban locations (Providence, RI; Tampa, FL; Detroit, MI; Seattle, WA) and six small city/rural locations (Puerto Rico; Keeney knob, WV; Cedar Rapids, IA; Grand Junction, CO; Rio Rancho, NM; San Jacinto, CA). While air toxics clearly is a problem of national scope, the problems are highly variable and dependent on local conditions (i.e., emissions mix, topography, meteorology).

Historically, as new monitoring needs develop (e.g., for new criteria pollutants, such as PM<sub>2.5</sub> in 1997), the focus is on that specific pollutant. The incentives for growth in ambient monitoring activities generally are clear and compelling and based on scientific findings that lead to revision of air quality standards or identification of important measurement gaps. Over time, these have generally been "layered" as one pollutant network upon another, such that we now have an ozone network, a PM<sub>10</sub> network, a carbon monoxide network, etc. Little thought or consideration has traditionally been given to integration of networks. At a time when resources are becoming more constrained, yet new air monitoring demands are anticipated, EPA, working with SLT tribal representatives, initiated a process to take a comprehensive and holistic look at the way air monitoring in conducted. This process has led to the development of the proposed National Ambient Air Monitoring Strategy (Strategy).

## 1.2 Purpose

The Strategy seeks to achieve an appropriate balance between needed stability and a desired improvement in response capability to scientific finding and emerging priorities. Assuming limited, at best, resource growth in monitoring programs, serious efforts must be devoted to optimize resources which can meet evolving monitoring challenges. Stability in networks is a positive attribute, as considerable time spans (decadal length) often are required to detect and interpret important air quality trends.

The capability to meet future monitoring needs is problematic given the current network structure.

Therefore, the primary purpose, or "goal," of the Strategy is to manage the Nation's air monitoring networks in a manner that addresses the most pressing public health issues, optimizes efficiency, and accommodates future needs, all within the constraints of the available funding.

#### 1.3 Strategy Development Process

The generation of findings and recommendations within this document was guided by the National Monitoring Strategy Committee (NMSC). The NMSC is a partnership committee among the EPA, and State/local and tribal representatives (SLTs). There are 18 members: seven EPA management level staff; seven representatives from State and local agencies, including the State and Territorial Air Pollution Program Administrators/Association of Local Air Pollution Control Officials (STAPPA/ALAPCO); three tribal representatives; and one facilitator. Since 1999, NMSC members have been meeting on a regular basis to provide the framework for the Strategy. To that end, this document represents the culmination, collectively, of many hundreds of hours of discussions, informational reviews, problem solving, issue resolution, and consensus building.

To support the effort, five technical workgroups were established to probe more deeply into specific components of the Strategy:

- (a) Formal workgroups (mix of staff from EPA and SLTs): These groups met as part of a major air monitoring Strategy meeting in October 2001 and have developed key components to the Strategy. The workgroups are as follows:
  - 1. Regulatory Review Workgroup (for modifications to 40 CFR part 58 monitoring regulations including changes in required number of criteria pollutant sites).
  - 2. *Quality Assurance Workgroup* (for modifications and recommendations for improved approaches and consistency in quality assurance programs).
  - 3. *Technology Workgroup* (for recommendations to accelerate dissemination of air quality data, and provide a review of EPA's continuous PM implementation plan)
- b) Two ad-hoc groups: These groups are linked peripherally to the Strategy development:
  - 1. *Network Assessment Workgroup* (technical staff from EPA and SLTs to review national assessment results; culminated in July 2001 workshop).
  - 2. *National Network Design Workgroup* (a small subset of NMSC members developing details on the proposed National Core network.)

There are also other existing groups which have had input and bearing on the activities of the NMSC. These are:

- (1) Air Toxics Monitoring Steering Committee a group of mostly NMSC members focusing on specific development of an air toxics monitoring program and using the overlapping responsibilities to ensure integration with the Strategy.
- (2) Clean Air Scientific Advisory Committee Particulate Matter Monitoring Subcommittee This group has been advising EPA on all aspects of particulate matter air monitoring. Over the last year an emphasis has been placed on implementing PM continuous monitoring which is a major operational element of this overall Strategy.

Together, the interactions of the committees and workgroups have successfully fostered a process which has substantially enhanced the efforts of the NMSC.

## 1.4 Operating Principles

Guiding the planning process is a handful of basic principles, agreed to by the NMSC, which form the foundation for the development of the proposed Strategy. These principles emphasize the active use of data and assessments, strong interactive communications, and incorporation of scientific advancements. Each are outlined below:

- (1) *Partnership*: EPA and SLT will jointly lead the planning effort underlying this Strategy.
- (2) "Zero-Sum" Resource Assumption: The Strategy is not a vehicle to add significant resources for air measurements. Relatively stable but flat spending is projected for air monitoring activities in the near future. This level-resource assumption can accommodate new air monitoring needs by targeting reductions in current monitoring, primarily for pollutants which are now well below the NAAQS. The Strategy does include some additional resource proposals (i.e., approximately \$12-15 million) required to catalyze certain technology and initial implementation elements of the Strategy. Furthermore, this Strategy intends to retain the basic infrastructure and operational stability of existing agencies. Reallocation implies shifts to different pollutant measurements and technologies, and not resource shifts across geographical regimes. Looking toward the longer-term future, a budget analysis process is warranted to assure that funding levels can sustain the Strategy.
- (3) <u>Flexibility by Balancing National and Local Needs</u>: Network design, divestment, and investment decisions must achieve a balance between prescription (consistency) and flexibility to accommodate national and local monitoring objectives, respectively. We must recognize that localized issues

are "national" issues, and nationally consistent data bases serve local (SLT agency) interests as well. A national strategy is enhanced by incorporating flexible processes to accommodate a spectrum of local and national objectives. Flexible principles must also be extended to reaching a balance between retaining valued stable network elements and introducing new elements that respond to new priorities.

- (4) <u>Institutionalize Network Assessments</u>: While this document incorporates results of broad based assessment of networks, assessments, especially at the regional level, should be performed on a regular basis to ensure the relevancy and stability of network operations.
- (5) <u>Demonstrate the Value of Data</u>: Data should be collected only following defined plans for its use, an associated commitment to objective analysis, and an understanding that collection of data determined to be valueless should be discontinued. A realistic understanding of data usage and patience must be exercised, recognizing that beneficial returns often require several years (e.g., identifying trends) of data collection. Implicit is the understanding that challenges to data usefulness must be answered at a minimum with a defined set of analysis plans and commitments. Clearly, if data do not undergo analysis, or plans for doing so are not available, one can only assume that the data have little or no value.
- (6) *Optimization Through Integration*: Monitoring programs often are administered on a program-by-program basis, an approach that does not foster active information flow across monitoring components or the development of truly complementary networks. The administration of programs should be in step with our understanding of the scientific and logistical linkages across programs. For example, the developing air toxics program should be considered an integration of existing programs (e.g., PAMS, PM<sub>2.5</sub>, State/local networks) combined with new initiatives. A wealth of complementary monitoring is performed by other Federal agencies (and other EPA programs) that support air quality program objectives and, in turn, benefit from the traditional program.
- (7) <u>Effective Interfacing with "Science</u>." An emphasis should be placed on more active engagement with the scientific community, and its products, recognizing the important role science plays in network design and technology and the role of networks in assisting scientific research. The perspective that a clear demarcation exists between science-oriented and agency-based monitoring is counterproductive to optimizing the collective value of research and air monitoring. A major cultural change that should be institutionalized is embracing the scientific community as a partner in planning and advice, as opposed to a limited role of critical review.

(8) <u>Minimize Adverse Program Impacts</u>: This Strategy should maintain integrity of existing agency monitoring programs by emphasizing shifts in programmatic areas (e.g., PAMS to toxics, PM<sub>10</sub> to PM coarse/toxics, etc.) and, if necessary, phase in gradual reductions in programs.

#### 1.5 Components of the Strategy

The Strategy is comprised of several key components, each of which is an integral and necessary element for success. These are described in greater detail in subsequent sections of this document. The components are:

- (1) a clear set of objectives as the foundation for the Strategy (Section 2);
- (2) the need and importance of periodic network assessments (Section 3);
- (3) the design of the National Core Network (NCore) (Section 4);
- (4) a review of quality assurance procedures and recommendations for more efficient quality assurance programs (Section 5);
- (5) a look at new air monitoring and data transfer technologies and how those can be incorporated into air monitoring networks (Section 6);
- (6) a review and understanding of monitoring capabilities (Section 7);
- (7) the regulation review process and what changes will be needed to enable the Strategy (Section 8); and
- (8) a communications and outreach program to ensure that agencies, community groups, business and industry, and the general public can be informed as to the benefits of implementing the Strategy (Section 9).

Most of these components are integrated and often co-dependent on each other. For example, national and regional assessments (Section 3) are conducted to provide broad national targets for implementing changes in existing criteria pollutant networks as defined by the objectives for the Strategy, as in Section 2.

#### 1.6 Recommendations

In proposing this Strategy, the NMSC is recommending several key changes to the way air monitoring is conducted. These changes will allow for more efficient collection of air quality data, more universal use of air quality data, and greater flexibility in air monitoring to meet the challenges of the twenty-first century in ways that meet both national and local monitoring needs. The recommendations are:

- (1) The atmosphere is a complex mixture of pollutants, and monitoring networks should include a greater level of multi-pollutant monitoring sites;
- (2) Continuous measurement technologies, for both gaseous and particulate pollutants, need to become the mainstay of monitoring networks;
- (3) The national "core" monitoring network (called NCore) should be able to address all the major demands of air monitoring networks, such as:
  - trend determinations;
  - reporting to the public;
  - assessing the effectiveness of control efforts;
  - providing data for health assessments;
  - determinations of attainment and nonattainment status;
- (6) The network should be flexible enough to meet local air monitoring needs, such as addressing environmental justice concerns, as well as national air monitoring objectives;
- (7) The network should improve the ability to rapidly communicate air quality data to the public, using features such as:
  - AIRNow;
  - State and local agency websites;
  - the media (especially TV and radio);
- (4) NCore should replace the existing NAMS/SLAMS network terminology;
- (5) NCore needs to incorporate scientific data needs to a greater extent than exists under the current network structure;
- (6) NCore structure should be three-tiered: [1] a backbone national multipollutant monitoring network; [2] an additional set of sites which can be single-pollutant to meet the monitoring needs for key pollutants of concern, such as ozone and PM<sub>2.5</sub>; and [3] a limited number of technically upgraded "supersites" which can accommodate scientific needs, such as new instrument testing; sampling of precursor and intermediate reactionary pollutants; and measurements of airborne biological particles;
- (7) There should be approximately 50 to 60 urban, and 10 to 20 rural "backbone" NCore sites. To the degree feasible, each State should have at least one of these sites;
- (8) Tribal participation should complement and enhance the network operated by State and local agencies;

- (9) Urban sites should be representative of urban-scale conditions, and therefore comparable among the urban areas;
- (10) Rural sites should be located so as to represent transport corridors, background conditions, or urban-rural couplet objectives;
- (11) The utilization of new technologies is strongly encouraged. NCore should be able to readily accommodate new technologies, both for air pollutant measurements and the rapid transfer of measured data to the public. Where measurement technologies are currently lacking, for example, the direct measurement of diesel particulate matter, research efforts should be encouraged;
- (12) There needs to be recognition that, for many criteria pollutants which are now well below the Federal NAAQS in many areas of the country (for example, carbon monoxide, nitrogen dioxide, sulfur dioxide, lead, and even PM<sub>10</sub>), our understanding of air quality conditions is well characterized. Further, there needs to be recognition that certain pollutants, such as air toxics and PM<sub>2.5</sub> are not well characterized. Based on our knowledge and need for protection of public health, there exists opportunities to reduce resources for those pollutants which are well characterized and increase resources for those pollutants which are not well characterized;
- (13) There needs to be a process whereby air monitoring networks undergo periodic assessments to determine if the existing network structure is optimally meeting national and local objectives. If not, the assessments should be the basis for network changes;
- (14) With the exception of the "supersites," the costs for establishing the NCore sites, including the local, flexible sites, should be covered from resource savings in reducing the number of monitors based on the network assessments;
- (15) Some elements will require targeted additional funding, including some capital costs for new equipment and establishment of the "supersites."
- (16) Recommendations for network changes should engage the public. A strong public communications program is advocated, both at the national and local levels;
- (17) In the establishment of NCore, leveraging of existing networks is encouraged to the degree feasible;
- (18) A review of existing regulations is needed to identify outdated requirements and enable NCore. Changes should be promulgated by EPA.

#### 1.7 Schedule

The development of the Strategy has taken almost 3 years. In trying to move forward in an expeditious manner, the following schedule has been developed:

Strategy Timeline				
Draft Strategy document for NMSC review	July 2002			
NMSC meeting for release of document	July 30, 2002			
Draft final document for public comment	Sept Oct. 2002			
Draft Regional network assessments	October 2002			
NMSC Review of Comments and Finalization of the Monitoring Strategy Document	January 2003			
Final Regional network assessments	March 2003			
CASAC review	Est: 2002-2003			
Outreach to science and environmental groups	2002 -2003			
Monitoring regulations proposal to NMSC	December 2002			
Monitoring regulations proposal in Federal Register	June 2003			
Monitoring regulations final	December 2003			
Deployment	2003 – 2007			

#### 1.8 Feedback

This document and the companion "Summary Document" are being made available for review and comment. Any comments should be submitted by November 22, 2002 to:

Ms Brenda Millar or e-mail:
U.S Environmental Protection Agency on fax:
Research Triangle Park, NC 27711 (919) 541-1903

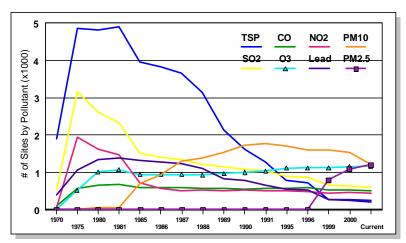
The NMSC will review comments prior to finalizing the National Ambient Air Monitoring Strategy Document.

## **Attachment 1.1 - Overview of the Existing Air Monitoring Networks**

The major routinely operating ambient air monitoring networks in the United States include a collection of programs primarily operated by States, local agencies and tribes:

State and Local Air Monitoring Stations (SLAMS) and National Air Monitoring Stations (NAMS)

SLAMS and NAMS represent the majority of all criteria pollutant (SO<sub>2</sub>, NO<sub>2</sub>, CO, O<sub>3</sub>, Pb, PM<sub>2.5</sub>, PM<sub>10</sub>) monitoring across the Nation with over 5000 monitors at approximately 3000 sites. These stations use Federal reference or equivalent methods (FRM/FEM) for direct comparison to the NAAQS. Design and measurement requirements for these networks are codified in the Code of Federal Regulations (CFR) parts 58 (design and quality assurance), 53 (equivalent methods), and 50 (reference methods). NAMS are a subset of SLAMS that are designated as national trends sites. The NAMS and SLAMS were developed in the 1970's with a major addition of PM<sub>2.5</sub> monitors starting in 1999 associated with promulgation of the 1997 PM NAAQS. These networks experienced accelerated growth throughout the 1970's with most components exhibiting declines in the number of sites with the exception of ozone and PM<sub>2.5</sub> (Figure A-1, and also Table 1). Rethinking the design of SLAMS/NAMS is a central topic of this Strategy.



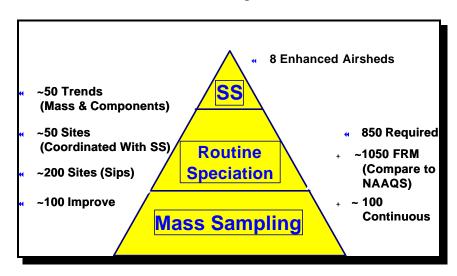
**Figure A1**. Growth and decline of criteria pollutant networks.

#### PM<sub>2.5</sub> networks

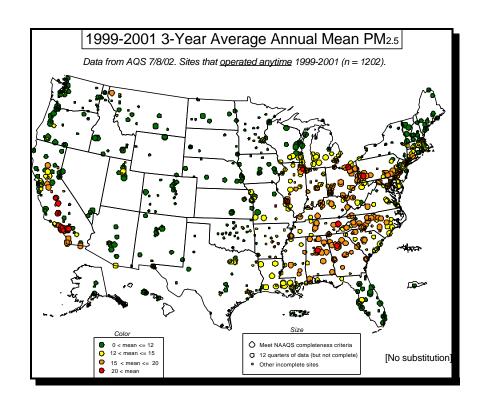
The PM<sub>2.5</sub> networks include three major components (Figure A2):

1) **mass only measurements** through nearly 1100 FRM filter based mass sites (Figure A3) that measure 24 hour averaged concentrations through gravimetry, and approximately 200 continuously operating mass sites using a range of technologies;

- 2) **chemical speciation measurements** that consists of approximately 50 trend, 250 State Implementation Plan (SIP), and 150 IMPROVE sites (Figure A4), respectively. The vast majority of these sites collect aerosol samples over 24 hours every third day on filters that are analyzed for trace elements, major ions (sulfates, nitrates, and ammonium) and organic and elemental carbon fractions. Most of the IMPROVE sites are operated by personnel from the Federal Land Management (FLM) and Forest and National Park Services. Over the last five years, these networks have been subject to reviews by the National Academy of Sciences (NAS), EPA's Clean Air Scientific Advisory Committee (CASAC), the General Accounting Office (GAO), and the Inspector General's Office. The CASAC review by the particle monitoring subcommittee has been engaged with EPA since 1999. Many of the recommendations related to the introduction of new methodology, particularly increased continuous particle monitoring and the corresponding need to redirect resources from FRM filter methods to continuous and speciation sampling have been addressed in detail through the CASAC subcommittee on particulate matter monitoring; and
- 3) **8 Supersites** executed as cooperative agreements with Universities and EPA that (city dependent) operate over various periods spanning 1999 to 2003 and conduct a wealth of standard and research grade measurements. Supersites are designed to address the extremely complicated sampling issues associated with fine aerosols and constitute an ambitious technology transfer and liaison effort across research level and routine network operations.



**Figure A2.** Overview of PM2.5 monitoring network elements.



**Figure A3**. PM<sub>2.5</sub> Federal Reference Monitoring sites.

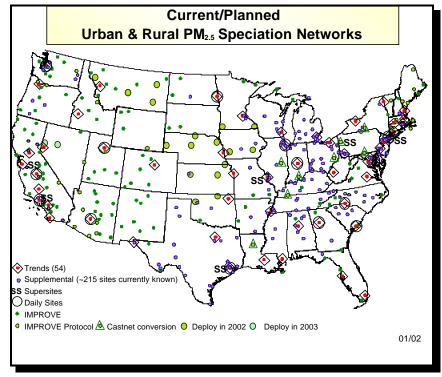
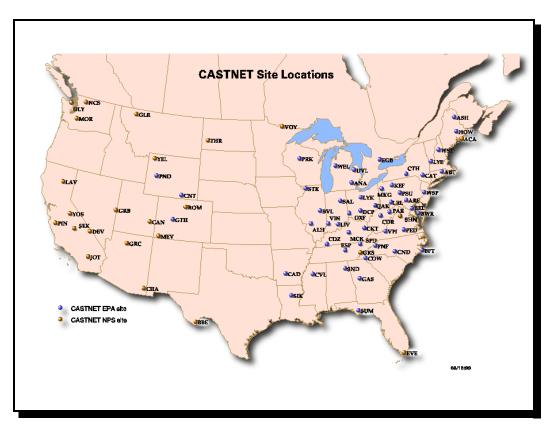


Figure A4.  $PM_{2.5}$  chemical speciation sites.

## **Clean Air Status and Trends Network (CASTNET)**

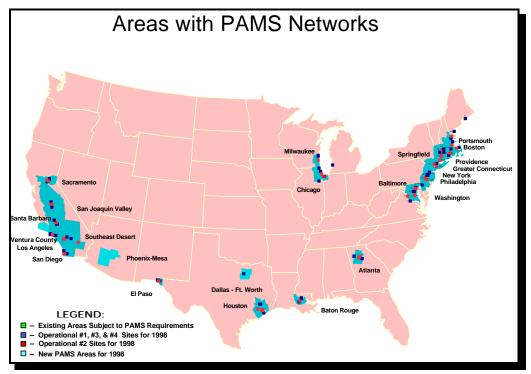
CASTNET originally was designed to account for progress of strategies targeting major electrical generating utilities throughout the Midwest which release acid rain precursor emissions, sulfur, and nitrogen oxides. Network operations are contracted out to private firms funded through Science and Technology (S&T) funds and managed by EPA's Office of Air and Radiation. CASTNET consists of approximately 70 sites located predominantly throughout the East with greatest site densities in States along the Ohio River Valley and cental Appalachian Mountains (Figure A5). Aggregate two week samples are collected by filter packs and analyzed for major sulfur and nitrogen oxide transformation compounds (e.g, end products such as sulfate and nitrate ions). CASTNET was deployed in the 1980's as part of EPA's National Acid Precipitation Assessment Program (NAPAP). A network assessment in the mid-1990's lead to a more optimized and less extensive network.



**Figure A5.** Clean Air Status and Trends Network (CASTNET).

## Photochemical Assessment Measurement Stations (PAMS)

PAMS measures ozone precursors {volatile organic compounds (VOC) and nitrogen oxides (NO<sub>x</sub>)} which react to form ozone at 75 sites in 25 metropolitan areas that were classified as serious ozone nonattainment coincident with release of the 1990 Clean Air Act (CAA) amendments (Figure A6). The addition of PAMS in the early to mid-1990's was a major addition (and burden to State and local agencies) to the national networks, introducing near research grade measurement technologies to produce continuous data for over 50 VOC compounds during summer ozone seasons. PAMS has been subject to numerous concerns regarding data quality and lack data analysis applications. More recent efforts have explored stronger linkage to air toxics monitoring as well as identification of more streamlined PAMS requirements (Chapter 4).

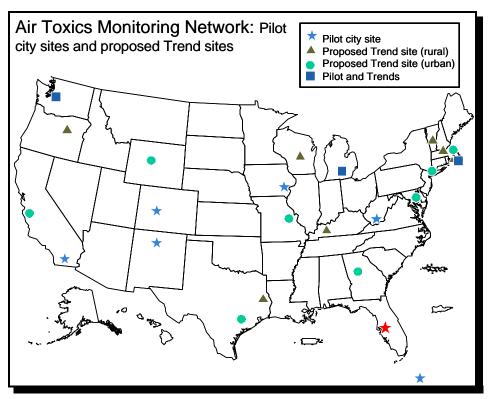


**Figure A6.** Photochemical Assessment Measurement Stations (PAMS) network.

#### **Air Toxics Monitoring Network**

Nearly 250 air toxics sites have been operated by State and local agencies largely through their own initiatives and funding as there are no Federal requirements for air toxics monitoring, and only recently have Federal Grant funds been earmarked for toxics monitoring. A steering committee consisting of EPA, State, and local agency members has been developing a National Air Toxics monitoring program. The program design effort is starting with a detailed analysis of data from existing sites and recently deployed pilot studies

(measuring 18 species) at four major urban locations (Providence, RI; Tampa, FL; Detroit, MI; Seattle, WA) and six small city/rural locations (Puerto Rico; Keeney Knob, WV; Cedar Rapids, IA; Grand Junction, CO: Rio Rancho, NM; San Jacinto, CA). While air toxics clearly is a problem of national scope, the problems are highly variable and dependent on location conditions (i.e., emissions mix, topography, meteorology). A majority of resources should be under the discretion of State/local agencies, and tribes to accommodate the variable and localized nature of air toxics across the Nation. A fraction of the program will support a national trends network that measures a limited number of species at perhaps 20-30 locations. Pilot city studies were initiated in 2001 to develop a consistent data base to support a national network design. The steering committee has recommended an initial 10- 20 urban and rural sites to start this network (Figure A7).



**Figure A7.** Air Toxics Pilot city sites and Proposed trend site locations.

## **Tribal Monitoring**

Tribal land monitoring (Figure A-6) continues to increase in the number of tribes that operate monitors and the number of parameters that are measured. As of August 2002, approximately 46 sites exist for which some data are report to EPA's AQS. This number will have reached approximately 50 by year's end 2002. Included in this number of 6 ozone monitoring sites; 24 PM<sub>10</sub> and PM<sub>2.5</sub> fine mass sites; 2 PM<sub>2.5</sub> chemical speciation sites. The sites also include a large number of accompanying meteorological measurements and several monitor for VOC and/or toxic chemicals. There are 2 existing IMPROVE fine mass speciation sites for regional haze measurements and 11 more sites should be added within the next year.

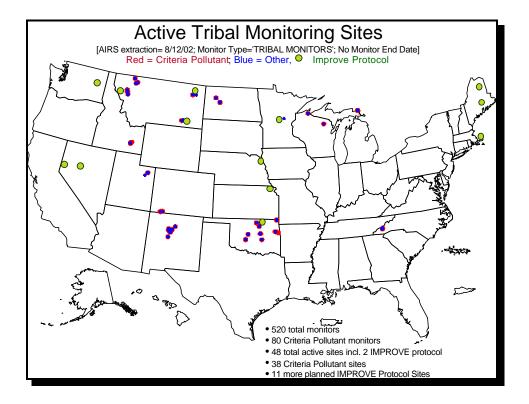


Figure A8. Tribal monitoring stations.

SLAMS/ NAMS	Approximate Current Number of Sites	% Measuring > 60% NAAQS	Historical High # Sites	Sampling Reporting Freq. (Year Found Unless Noted)	Notes
Ozone	1167	> 80 (8 hr)	1167 (2002)	hourly (May - September)	
PM2.5	1200	>75	1200 (2002)	24-hr average; mix of daily, every third day and every sixth day	
PM10	1214	< 25	1763 (1991)	mix of 24-hr. Avg., every sixth day; and hourly	
SO2	592	< 5	3158 (1975)	hourly	
NO2	437	< 5	1944 (1975)	hourly	
CO	498	< 5	684 (1981)	hourly	
Pb	247	< 5	1393 (1981)	24-hr. Avg., every sixth day	
TSP	215	NA	4894 (1981)	24-hr. Avg., every sixth day	
PM2.5					
FRM mass	(1100)				as above
Continuous mass	200	NA		hourly	
Speciation	54 trends; 160 SIP, 140 IMPROVE	NA		mostly 24-hr. Avg.; every third day	major ions (sulfate, nitrate, ammonium); carbon fractions (organic and elemental); trace metals
<u>PAMS</u>	77 sites in 25 MSA's	NA		mix of hourly, 3-hr. Avg. and 24-hr. Average (56 VOC's, TNMOC and carbonyls throughout ozone season	ozone and NO2 include in SLAMS/ NAMS
<u>Toxics</u>	280 (10 National pilot sites)	NA		broad range of metals, VOC's, SVOC's; Pilots: 18 species (metals, VOC's, aldehydes); 24-hr. Avg., every sixth or twelfth day	
CASTNET	70	NA		total nitrate, sulfate, ammonium 2-week avg. samples	ozone and IMPROVE measurementsinclud

## Section 2. Objectives

The NMSC established key elements to the Strategy which it deemed to be crucial to an effective program. These included a set of objectives (e.g., what the Strategy is intended to accomplish, as delineated in the Section 2.1, below), specific components (e.g., what are the key functions that need to occur [presented in Section 1]), attributes to some of the components (e.g., what the components are intended to accomplish, as given in Section 4), and an overriding set of operating principles (e.g., what are the constraints which must be considered [presented in Section 1]). Together, these formed the complete framework for the Strategy, from which the details evolved.

## 2.1 Objectives for the Strategy

The NMSC has developed 12 objectives for the Strategy, as follows:

- To manage the Nation's air monitoring networks in a manner that addresses the
  most pressing public health issues, optimizes efficiency, and accommodates
  future needs, all within the constraints of the available funding.
- To establish a new air monitoring paradigm coupling a minimum level of required national monitoring with flexible SLT air monitoring networks in order to efficiently and effectively meet both national and SLT needs.
- To provide a greater degree of timely (e.g., real-time) public air quality information, including the mapping of air pollution data and air quality forecasts.
- To promote network efficiencies through the reevaluation of regulations and quality assurance procedures.
- To foster the utilization of new measurement method technologies.
- To provide a mechanism for the periodic assessment, from both a national and local/regional perspective, of all air monitoring activities to help ensure the relevance and efficiency of the network. (This mechanism should provide appropriate flexibility to disinvest in monitoring activities should changing priorities so warrant.)
- To encourage multi-pollutant measurements, where appropriate, for better air quality management and scientific/health-based data sets.
- To provide a base air monitoring structure which, in conjunction with special studies (not part of this Strategy), could be used to support certain regulatory needs, e.g., SIP development, source apportionment, operational model evaluation, and tracking progress of emissions reduction strategies.

- To develop and implement a major public information and outreach program as an important cornerstone toward network changes.
- To seek input from the scientific community as to the merit/value of proposed changes.
- To provide air monitoring platforms and data bases which can be used for other environmental purposes, such as area-based ecosystem assessments, global issues, diagnostic research, and biological sensing.
- To assess, periodically, funding levels needed to maintain support for this
  monitoring strategy, and incorporate recommendations into the budget planning
  process.

## 2.2 Basic Network Objectives

The Strategy encompasses many elements, though the air monitoring portion is the central component. Therefore, the national monitoring strategy requires a clearly defined set of network objectives as a foundation for assessing current networks, establishing monitoring priorities, and articulating a vision for future direction. These objectives are more focused on the actual use of ambient data, in contrast to the wide spectrum of objectives associated with the monitoring strategy, as specified above. Monitoring data provide value to air quality planning, the public, and other information users, such as the research, academic and business/industrial communities.

Ambient data from the regulatory-based networks administered primarily through the Federal CAA section 105 and 103 grant process should address a variety of air quality program needs that include:

- **Compliance:** Comparing air quality data to NAAQS or other benchmarks which drive regulatory actions. For example:
  - determining attainment/nonattainment status
  - establishing baseline and progress measures for regional haze
- **Public awareness/population exposure**: Data to support the air quality index (AQI) and AIRNow, and population risk and exposure assessments. For example:
  - providing timely information to the media
  - forecasting pollutant conditions
  - relating risks to health benchmarks for hazardous air pollutants
  - providing data in response to environmental justice and related public issues

- evaluating air quality simulation models for assessing impacts to the local population
- Detecting air quality trends and evaluating progress of emissions reduction programs: Data to detect long term air quality trends and to capture measurable ambient impacts (including emissions precursors and secondarily formed pollutants) associated with emissions reduction programs. For example:
  - assessing accountability for progress toward cleaner air
  - determining the effectiveness of regional haze mitigation efforts
  - understanding visibility-impairing components to regional haze for adequate progress assessments
  - determining if permitting requirements are sufficient to meet rate-ofprogress or maintenance-level commitments
  - reporting of trends data to the public
- Emission strategy development: Data to support construction of emission reduction programs in support of State Implementation Plans (SIPs), air toxics and environmental welfare/secondary effects programs (e.g., visibility impairment, watershed degradation). [Note: This objective, although similar, is delineated from the previous objective, as the types of monitoring approaches often are specific to the tool (e.g., model) being applied. In many instances, emphasis is put on a short term (e.g., up to 1 year) period of data collection to support model applications, whereas trends and program evaluation almost always demand a long term data record.] For example:
  - supporting source-apportionment and other observational models
  - evaluating simulation models for predicting future air quality
  - defining background, transport, and model boundary conditions
  - evaluating emission inventories
  - assisting in the determination of multi-media (e.g, air, water, and soil) impacts of pollution
- **Research**: Data to assist research programs. [Note: Research support is not a primary objective of the Nation's regulatory networks. However, the regulatory networks provide an important infrastructure that often is leveraged with other research resources that benefit air quality research and eventually regulatory programs.] For example:
  - developing associations between measurements and adverse health indicators
  - describing physical/chemical processes
  - testing and evaluating advanced sampling methods
  - supporting studies on health effects and human exposure
  - supporting development of advanced simulation models
  - supporting the better understanding of atmospheric processes

## 2.3 Relationship to Existing 40 CFR Part 58 Monitoring Regulations

The existing monitoring regulations also list a set of objectives, located in the Code of Federal Regulations (CFR) 40 part 58, Appendix D for the existing SLAMS network, of which the NAMS are considered a subset. These include:

- determining highest concentrations
- determining representative concentrations
- determining impact on ambient levels due to emission sources
- determining regional transport
- determining welfare-related impacts in rural areas

In addition, the CFR lists several objectives for PAMS:

- for NAAQS attainment and control strategy development
- for SIP control strategy evaluation
- for tracking emissions
- for determining trends
- for identifying airshed boundary concentrations
- for air quality model evaluation
- for ozone and air toxics exposure

These objectives for the combined NAMS/SLAMS/PAMS networks are consistent with those articulated previously, illustrating stability and confirmation in the basic uses and purposes of monitoring data. Although consistencies exist between the objectives stated in Section 2.1 and the regulations, the revised objectives provide a more tractable and realistic group of expectations that incorporate more recent thinking on monitoring science. (For a more detailed discussion of changes to regulations in support of the Strategy, see Section 8.)

#### Section 3. Network Assessments

This section includes an overview of the assessment process, the national assessment results, and the role of regional assessments.

## 3.1 Role of Monitoring Network Assessments

Specific monitoring needs typically dictate the establishment of new monitoring sites. These may be Federal requirements for establishing a specific number of samplers for a specific pollutant; needs for meeting SIP data requirements; determining the impacts of local sources; determining background or transport conditions, to name a few. There are many more reasons why air monitoring sites are established. Once established, though, these sites take on a sense of perpetuity, in general, with little follow-up action to determine if the original intent is being met, or perhaps completely fulfilled. Also, changes in air quality conditions over time may change the representativeness of a particular site. For example, if a site were selected to represent the maximum concentration with an area, and growth, changes in emissions, and other factors have changed the location of the maximum concentration, then that site no longer fulfills its intended purpose.

To assure that monitors are meeting their intended purpose, and that associated resources needed to maintain those sites are being utilized most efficiently, a periodic review, or assessment, of an air monitoring network is necessary. Such review can be done on a national basis (to examine the adequacy of monitors to meet national monitoring objectives), or on a regional basis (to determine if regional pollutant conditions are being adequately addressed), or on a local basis (to determine if local monitoring needs are being met). EPA requires annual network reviews on a local basis, but typically these reviews are cursory in nature, without a formalized approach toward determining if indeed the network is optimized.

As part of the Strategy, network optimization is desired, and hence, an integral part of assuring ongoing optimization is the establishment of formalized periodic network review. On a national basis, it is recommended that such reviews be done on a 5-year cycle – the same time interval as required under the Clean Air Act for the review of the NAAQS. Because regional and local conditions may be more varied, it is recommended that regional/local network assessments be conducted on a 2-3 year cycle.

A national assessment was recently conducted and the results made available in 2001. Although a few EPA regions have already conducted a regional assessment, it is intended that all EPA regions complete an initial network assessment by the end of 2002. These regional assessments can be conducted in conjunction with local assessments. The intent is to have an initial "physical checkup," so to speak, of the Nation's air monitoring networks at a time when the implementation of the Strategy would be expected to begin.

#### 3.2 The National Assessment

The national assessment was motivated by an understanding that certain aspects of the national networks largely had served their original purpose and were not optimally designed to meet current and emerging monitoring needs (e.g., continuous particulate matter and air toxics). The objectives for this assessment were twofold: (1) to produce an objective evaluation of the relative value of current monitoring sites for identifying broad national targets in terms of monitoring sites that could be discontinued because of limited value of the data provided; and (2) to provide a catalyst for more refined regional and local analyses that are needed to implement actual site-based changes in the network and to generate consensus for priority investment areas in other monitoring programs. This assessment represents the first objective comprehensive evaluation covering the majority of the Nation's regulatory ambient air monitoring stations operated largely by state and local agencies. All criteria pollutant networks, including ozone, carbon dioxide, sulfur dioxide, nitrogen dioxide, lead, PM<sub>10</sub>, and PM<sub>25</sub> were addressed in this study. The other major ambient monitoring program operated by State and local agencies, PAMS, is undergoing a parallel assessment which will be integrated with the results of criteria pollutant network assessment as part of the Strategy.

#### 3.2.1 Methods

The assessment approach incorporated a combination of objective and subjective elements that were based on methodology developed by Washington University (Husar, 2000) and complemented by an ad-hoc assessment workgroup that developed a protocol and provided ongoing advice related to measures and objectives considered in the array of assessment analyses. Details regarding the method are found in <a href="http://www.epa.gov/ttn/amtic/monitor.html">http://www.epa.gov/ttn/amtic/monitor.html</a> under *Preliminary outputs from the National Network Assessment Introduction and Explanation-File #1.* The analytical approach consisted of developing five independent measures that could be grouped to reflect the ability of a given monitoring site to meet a specified monitoring objective. The measures included:

- 1. Concentration
- 2. Spatial representation
- 3. Population
- 4. Measurement uncertainty
- 5. Deviation from the NAAQS

All monitoring data were ranked from highest to lowest according to these measures, and aggregated in spreadsheets to allow for post-processing. Data were grouped by concentration as they relate to the NAAQS. The post-processing involved direct graphical displays of quartile groups for each measure on a pollutant-by-pollutant basis, and grouping of measures with variable weighting schemes (Table 3) to represent more specific monitoring objectives. The selection and weighting of these measures was documented in the protocol and refined over a series of conference calls with members of the assessment workgroup. Each monitoring site for a given criteria pollutant was ranked

across all monitoring sites and graphically displayed (**see Attachment 3.1**) in quartiles where the upper 25% (color red) represented most important locations for the measure considered (e.g., highest 25% concentrations, 25% sites with greatest uncertainty, most populated sites) and the lower 25% (color blue) represented the least important sites based on the particular measure. Summaries of the quartile results are provided for each EPA region. In addition, the recent 5 and 10-year trend directions (up, down, not significant) for each pollutant are provided to complement the group of measures used in the assessment.

Table 3. Weighting schemes and objectives.								
	Concentration	Uncertainty	Deviation from NAAQS	Area	Population			
W1: equal weights	20%	20%	20%	20%	20%			
W2: NAAQS Compliance	30%	30%	30%	5%	5%			
W3: exposure/AQI	30%	5%	5%	30%	30%			
W4:	50%	50%	0	0	0			
W5: emissions tracking/model evaluation	20%	40%	0	40%	0			

#### 3.2.2 Role of the NMSC

Any combination of measures and weights can be applied to the ranked data. The weighting schemes are based on input from the assessment workgroup that were believed to reflect general objectives developed by the NMSC. The particular grouping and weighting of measures is a subjective process that requires input from the NMSC. What combinations of measures and weights that reflect the recommendations of the NMSC? Note, that any combinations of measures can be aggregated as a simple post processing exercise.

#### 3.2.3 Role of EPA Regional Offices and SLTs

All EPA Regional Offices, in conjunction with the States, Tribes, and any multistate organizations in that region, are expected to undertake a regional/local assessment to complement the national assessment. These regional/local assessments should be completed by the end of 2002 and delivered to EPA OAQPS, and should include an interpretation of the national assessment as it affects their region. The regional/local assessment should also include proposed regional/local network modifications that are either consistent with this assessment or reflect more refined assessments conducted for their region. In the absence of a regional/local assessment for a given region, OAQPS may need to rely on the results of the national assessment (and, perhaps, the results of

other regional/local assessments) to develop proposed network modifications for that region.

#### 3.2.4 Role of EPA

The regional/local scale assessment work is not likely to address the ability of networks to characterize broad regional/national scale issues. Examples include background concentration levels and transport characterization. EPA should identify the monitoring required to meet larger scale "national" needs to ensure adequacy of monitoring and reduce the risk of removing "valuable " monitors that are undervalued from a local perspective. There needs to be close coordination among OAQPS, the EPA Regional Offices and the SLTs to achieve valued results. EPA will coordinate this design activity as part of the Strategy.

## 3.3 Summary of Results

A complete compilation of results can be located in <a href="http://www.epa.gov/ttn/amtic/monitor.html">http://www.epa.gov/ttn/amtic/monitor.html</a> under <a href="Preliminary outputs from the National Network Assessment Results Files #1 and #2">http://www.epa.gov/ttn/amtic/monitor.html</a> under <a href="Preliminary outputs from the National">Preliminary outputs from the National</a> are simply graphical summaries of the ranked data taken directly from the data base <a href="http://www.epa.gov/ttn/amtic/monitor.html">(http://www.epa.gov/ttn/amtic/monitor.html</a> under <a href="Preliminary outputs from the national Network Assessment Pollutant site files in Excel format">Preliminary outputs from the national Network Assessment Pollutant site files in Excel format</a>). The Results File Number #2 includes mappings of the combined measures as well as additional analyses illustrating trends patterns and maps depicting sites relative to the NAAQS levels.

#### 3.3.1 Caveats

It is important to remember the limitations of this national top-down analysis. As noted earlier, from a procedural perspective, the national assessment must be complemented by more refined local and regional assessments to derive input from stakeholders and produce site-specific recommendations. From a technical perspective, the national top-down approach works well for certain pollutants and/or objectives, but falls short in other areas. For example, evaluating the "value" of ozone monitors located in New Jersey with Washington State monitors (and many other examples) can create an impression where ozone monitoring is only useful in high concentration regions of the country. A better approach is to review the ozone network of the Northwest and rank the value of ozone stations within particular regions where regional differences in setting the priority of monitoring objectives are expected. The national assessment is severely compromised by not considering site-specific spatial scales of representation. In attempting to illustrate value of monitoring sites for model evaluation and related needs, weighting scheme W5 (Table 3) emphasized those sites located in rural or isolated urban areas with the implicit assumption that such sites represent broad spatial areas. While

this approach may work well for  $PM_{2.5}$  and perhaps ozone, the approach is compromised for CO and  $PM_{10}$ , which often are sited to capture maximum local scale impacts. Again, important details simply are not captured in a broad national analysis, and misleading conclusions at the site can easily occur. Sites with high concentrations generally tend to be weighted very high, a result that mistakenly could imply a lack of importance for background and related monitoring sites.

#### 3.3.2 General Interpretations

Clearly, two criteria pollutants, ozone and  $PM_{2.5}$ , dominate the Nation's air quality with respect to elevated concentrations. This conclusion is reflected in the NAAQS proportion maps. (See Attachment 3.1.) When considering the suite of maps presenting quartile breakouts, one must consider that the top 25% of  $PM_{10}$  sites are not as valued as the top 25% ozone sites, and this logic filters through the remaining quartiles as well. These results reinforce our general understanding of the surplus of monitoring sites for criteria pollutants for which substantial progress has been achieved in reducing concentrations of CO,  $SO_2$ ,  $NO_2$ , Pb and  $PM_{10}$  over the last 20 years.

Considerable attention must be paid to both the ozone and PM<sub>2.5</sub> results due to a variety of policy and technical complexities. These results attempt to view the relative value of monitoring sites based on objective criteria that are largely decoupled from existing or future constraints due to policy considerations. For example, an ozone site rated "low" value due to some combination of measures may not be a viable candidate for removal due to established agreements requiring a monitor in a certain county, or to track a record of continued non-exceedance readings to meet maintenance plan or related SIP requirements. The PM<sub>2.5</sub> network presents a unique case where the network has just been deployed and already discussions on major modifications are taking place. The motivation for change is based on several factors including recommendations from the research community to emphasize continuous PM measurements and State and local agencies requests to reduce operational burden associated with filter-based measurements. The generally observed homogeneous behavior over space and time of PM<sub>2.5</sub> levels in broad regions of the East and Midwest suggests the network can absorb site reductions with little risk in compromising the ability to meet network data use objectives, especially with a subsequent introduction of continuous PM instruments that produce acceptable data quality.

#### 3.3.2.1 Ozone

From a national perspective, a minor reduction in the number of ozone sites (e.g. from urban clusters) is recommended. This reduction in the current network would not compromise our ability to address NAAQS compliance, provide input for public reporting needs (AQI, AIRNow) or assess effectiveness of emissions control programs, including evaluation of air quality models. All of these objectives would be better served by using any resource gains from such a reduction to position ozone

monitors in areas with current "high" measurement uncertainties, locations typically outside the existing MSA of interest. The relocation should be guided by considering results of interpolated error regimes (e.g., Attachment 3.1, Figure 12), air quality model output indicating expected spatial gradients and the collective knowledge of local monitoring experts that can address the logistics of site procurement and operation.

Ozone assessments were performed on both 1- and 8-hour averaging periods, as well on two databases, 1995-1997, and 1998-2000, to address policy issues associated with both ozone NAAQS. Obviously, the form of the NAAQS greatly impacts an interpretation of ozone compliance across the country, as the 8-hr NAAQS extends exceedance locations beyond the classic urban corridors observed for 1-hr NAAQS in the Northeast, Southwest (e.g., Los Angeles, Houston, and Dallas) and Chicago, to broad regions throughout the East, Midwest, and California. Obviously, modifications of the ozone network must be conducted with caution given the broad spatial extent of elevated ozone levels nationally. Nevertheless, examination of the assessment results suggests areas for optimization within the ozone network, which was established in large part to address the 1-hr NAAQS. This has resulted in a network strongly emphasizing clustering of urban sites. The newer 8-hr standard suggests that rural/regional locations take on more "relative" importance than that associated with the 1- hr NAAQS. In addition, an enormous body of scientific evidence and associated advice (NRC, 1991; NARSTO, 2000), as well as movement of populations away from urban centers to expanding suburbs and rural locations, supports an increased emphasis on rural/regional ozone monitoring. The Southeast includes several upward-moving ozone 8-hr trends over the last 10 years, consistent with population growth across the South. All major metropolitan areas with clustered ozone sites should consider removing those sites that provide only minimal relative value compared to other sites in the cluster. Examples include Chicago, major Eastern cities (e.g., New York, Boston, Philadelphia, Pittsburgh, Baltimore-D.C) and major California cities. Such inference should be tempered by the need to retain some core of low level background and spatial gradient sites for model evaluation and transport analyses. Consideration should be given to identifying even remote locations to provide more complete spatial detail nationally and consider enhancing partnerships with other Federal agencies (NPS, USFS) and Tribes to address areas with major geographic gaps.

#### 3.3.2.2 PM<sub>2.5</sub>

From a national perspective, a significant reduction in the number of PM<sub>2.5</sub> FRM monitors is recommended. This reduction in the current network would not compromise our ability to meet the principal data quality objective of addressing NAAQS compliance. It is assumed that the existing FRM network will be maintained through the end of 2002 or until three full calendar years of data are collected, whichever is later. (The only exceptions to this might be to: (1) relax the sampling frequency to 1-in-6 day at sites where the annual NAAQS is controlling, and (2) eliminate low concentration, redundant FRM monitors, if resources are needed now to

support deployment of speciation or continuous monitors. After the end of 2002, or when three full calendar years of data are available, then a significant reduction in the number of FRM monitors to something on the order of 700 – 800 sites nationally should be considered. Because the FRM filter-based technology will not, however, meet the needs for timely data reporting (e.g., AQI and AIRNow), a substantial effort must be put forth to implement continuous PM monitors that produce acceptable data quality into the network to meet multiple data analyses. Eventually, the number of integrated FRMs can be reduced further in parallel with the incorporation of PM continuous instruments that produce a successful record of meeting specified performance standards. EPA must accelerate the production of guidance for identifying redundant FRM sites for removal, the development of DQO's and performance standards that will facilitate introduction of continuous methods, and associated regulatory changes to accommodate these technical adjustments.

The perspectives and recommendations presented here are based on those assessments addressing the annual PM<sub>2.5</sub> data aggregate, as the annual standard is the dominant controlling factor throughout most of the Nation. While it may appear premature to consider modifications in such a recently deployed network, a rethinking is in order given: (1) the enormous operational burden placed on monitoring agencies, (2) advice and direction provided by CASAC and the NAS, and (3) recognition that any program has room for improvement. Due to the initial design objectives emphasizing "representative" siting (as opposed to capturing only "hot spot" signals) as well a generally coherent behavior of fine aerosol concentrations, the PM<sub>2.5</sub> network provides, perhaps, the most statistically solid basis for conducting network assessments. As anticipated, there exist broad regions of consistent behavior of fine aerosol which implies opportunities for removing sites without compromising the ability to characterize regional and local aerosol patterns. Despite evidence indicating the potential for broad extent of PM<sub>2.5</sub> nonattainment through the southeast and parts of the Midwest (Attachment 3.1, Figure 2), several potential sites should be considered for removal and/or subsequent replacement with continuous PM monitors (Attachment 3.1, Figures 15 and 16). Every region of the country should review their PM<sub>2.5</sub> FRM networks and identify "redundant" sites as candidates for removal/replacement. Although the PM<sub>2.5</sub> sites are not as highly clustered as those in the ozone network, population density generally drove PM<sub>2.5</sub> network design with expected site redundancies in urban locations. In addition, several areas of the country including New England, upstate New York, Florida and much of the North Central States and West, outside California, do not exhibit elevated PM<sub>2.5</sub> concentrations (Attachment 3.1, Figures 2 and 17). Those areas should review their network paying careful attention to optimizing sites that emphasize characterizing background and gradient patterns and public reporting more than NAAQS compliance. EPA should provide a recommendation based on the national need for characterizing background and gradient PM<sub>2.5</sub> levels and determine what adjustments are

<sup>&</sup>lt;sup>1</sup>Note that the FRM network provides an excellent base for characterizing spatial patterns of PM<sub>2.5</sub> nationally. This ability to provide such characterizations should not be compromised as modifications emerge.

needed to the combined Speciation/IMPROVE and PM<sub>2.5</sub> mass networks are needed to best serve evaluation of national air quality models.

## 3.3.2.3 PM<sub>10</sub>

A major reduction in the number of  $PM_{10}$  monitors is recommended. Only those sites that have current  $PM_{10}$  exceedances and violations, as well as those required as part of SIP approval conditions should remain as priority sites. Any additional  $PM_{10}$  monitoring should be conducted at locations collocated with a  $PM_{2.5}$  FRM, with suspected "elevated" PM-coarse concentrations, and with measurement technology compatible with the  $PM_{2.5}$  FRM. Clearly, opportunities for reduction are far greater in eastern regions of the country (Attachment 3.1, Figure 17).

Monitoring for  $PM_{10}$  continues at over 1000 sites nationwide with a very small number of exceedances (Attachment 3.1, Figure 7) for a pollutant that is being phased out of the air program. Clearly, the consumption of resources dedicated to  $PM_{10}$  monitoring is not in phase with the current importance of the  $PM_{10}$  problem. Although EPA is likely to promulgate a coarse PM standard ( $PM_{10}$  -  $PM_{2.5}$ ), the variety of  $PM_{10}$  monitoring methods generally is not consistent with the method requirements that will emerge from a  $PM_{coarse}$  NAAQS.

#### 3.3.2.4 CO

A major reduction in the number of CO monitors is recommended. Only those sites that have current CO exceedances and violations, as well as those required as part of SIP approval conditions should remain as priority sites. Existing CO monitors located in urban microscale sites should be relocated to more broadly representative urban locations. In addition, CO monitoring should be conducted using high resolution instruments in rural areas to provide regional information about CO concentrations, as may be needed to evaluate air quality models and apply observation-based methods (OBMs).

The CO assessment is complicated by predominant microscale influences arising from busy traffic intersections, urban canyon effects and other factors that lead to maximum concentrations observed within the very close proximity of sites. Network design for CO should undergo a major transformation to address other data analysis needs including air model evaluation and observational based approaches (e.g., source-receptor modeling, OBMs). This shift would require investing in high resolution CO monitors capable of capturing background concentrations and locating instruments in areas representative of general background concentrations and within expected gradients. This undertaking also should be incorporated as part of the overall monitoring strategy addressing future network design.

#### 3.3.2.5. SO2

A major reduction in the number of  $SO_2$  monitors is recommended. Only those sites that have current  $SO_2$  exceedances and violations, as well as those required as part of SIP approval conditions should remain as priority sites. Any additional  $SO_2$  monitoring should be conducted at a small select number of sites to address 5 minute averaging times in response to concerns regarding short-term  $SO_2$  exposures and in rural areas to provide regional information about  $SO_2$  concentrations, as may be needed to evaluate air quality models.

As a major precursor for PM<sub>2.5</sub>, very little relevant SO<sub>2</sub> data exist that allows for evaluation of air quality models or for the support of observational methods that rely on formation rate principles. (In this consideration, CO and N species are also useful.) Investments in SO<sub>2</sub> should be made in monitors capable of reading background concentrations and siting in areas with larger spatial scale representativeness collocated with other coupled atmospheric process and health related measurements.

## 3.3.2.6. *NO*<sub>2</sub>

A major reduction in the number of  $NO_2$  monitors is recommended. While there remains a need to track national trends, the network must undergo major modification to address the more important needs associated with tracking control program progress for ozone,  $PM_{2.5}$ , and model evaluation. This suggests the need for sites in rural areas to provide regional air quality information, and to establish monitors for NO/NOy, which is a better indicator than NO/NOx.

The NO<sub>2</sub> network no longer is required for the primary purpose of NAAQS. Changes need to be made in monitoring methods, as NO<sub>2</sub> is a poor parameter to track emissions that emerge first as NO and are gradually oxidized to an aggregate of species collectively referred to as reactive nitrogen, NOy. Technology for high resolution NOy (which simultaneously measures NO) is available and some limited progress has been made in developing an NOy/NO network, although significant quality assurance issues associated with calibration exist. However, a network for assessing the effectiveness of major nitrogen emission reductions currently is not in place. Note that some of the existing NOx/NO monitors located in representative emission areas, such as PAMS sites, do provide some ability to track emissions in urban areas. Because many of the major nitrogen oxide sources are located in non-urban locations, and because of the broad extent and dilution of emission plumes (and propensity for "urban" noise to wash out signals), a regional rural NOy network is probably required to detect long-term changes in nitrogen species emissions associated with major utility source reductions. Note that NO<sub>2</sub> as a measurement offers incredible value for model evaluation at the diagnostic level, as NO, is involved as a key parameter in so many chemical pathways. Unfortunately, there does not exist an affordable solution for routine monitoring of NO<sub>2</sub>. Current NO<sub>2</sub> measurements are influenced by measurement artifacts that generally produce a positive bias in the measurement. Fortunately, the relatively fresh emissions in urban locations where NO/NOx monitors are sited generally result in plumes dominated by NO where artifacts due to oxidized products are somewhat minimized. The use of current technology in rural locations is not appropriate as the aged plumes contain a greater percentage of oxidized nitrogen that will bias the NO<sub>2</sub> calculation, and the concentrations in rural locations are below the resolution limits of commonly used NO/NOx monitors.

#### 3.3.2.7. Lead

A major reduction in the number of lead (Pb) monitors is recommended. Only those sites that have current Pb exceedances and violations, as well as those required as part of SIP approval conditions should remain as priority sites.

Progress in the reduction of lead concentrations is a clear air program success story. Basically, we should declare victory and limit lead monitoring to those isolated areas influenced by significant stationary sources, and maintain those sites identified by EPA to retained for long term trends.

# 3.3.3. Recommended Analysis and Related Activities

The national analysis served a necessary role in confirming a prevailing view of a two criteria pollutant problem, ozone and PM<sub>2.5</sub>, in the United States. Accordingly, the assessment clearly indicates that major reductions in most other criteria pollutant monitoring programs are in order. The national assessment also appears to corroborate more detailed assessment work conducted by participants in the North Central States. Nevertheless, the national assessment work could be improved to better service both national and regional needs. Based on the July 2001 network assessment workshop and input from the assessment workgroup, a number of suggested improvements to the national assessment and advice for subsequent regional/local assessments include:

- 1. **Emphasizing the importance of regional assessments**. The national assessment results provide conclusions that may apply on a national scale, but could be misused at a regional level. For example, clustered monitoring sites in general may produce "low value" data, yet in certain areas such data are used for an array of objectives and would be classified as "high value" when approached with a more resolved perspective.
- 2. Regulatory and programmatic changes which must accompany assessment results. The assessments produce technical recommendations that could impact monitoring. Specific changes in EPA Grant guidance and monitoring regulations are needed to support investment in new monitoring programs and divestment in identified programs.

- 3. Improving spatial scale representativeness of monitoring sites. The current polygon data analysis procedure accurately portrays a nearestneighbor concept where the defined area incorporates every point closest to the monitor. This approach is analogous to identifying the closest fire station to a residence, an intuitively useful notion that associates the closest monitor in space to the enclosed population. The polygon methodology is developed solely through a geometrical construct and does not account for topographical and meteorological factors which influence actual spatial zone of representative for a particular monitoring site. Improvements in the "area" measure and those objectives that consider this measure, particularly model evaluation, would increase the applicability of the assessment at both the national and local level. Each EPA Regional Office is requested to review and rank all monitoring sites with respect to actual spatial representativeness through the type of methodology provided by EPA Region 5. These revised rankings will be reapplied by EPA OAQPS in further iterations of the assessment requested by the EPA Regional Offices. During an interim period, EPA OAQPS will rerun selected weighting schemes with a reduced emphasis on the "area" measure.
- 4. **Including special event data**. To retain an ideological and technically sound approach, all data sources should be utilized in the assessment. Instances where exceptional events data were excluded should be noted in appropriate tables and figures.
- 5. Applying the assessment at regional scales with separate weighting schemes. Each region/interstate group should develop a weighting scheme indicative of the objectives more closely associated with that region, and the assessment recalculated for specific regions. EPA OAQPS will perform regional assessments based on more specific input provided by EPA Regional Offices.
- 6. **Performing more critical review of results**. The reliance on graphs indicating quartile breakouts may overlook natural breaks in the data that suggest more obvious delineations for "high" and "low" value sites. In addition, some normalization could be achieved by considering values of scores as opposed to only ranked order when combining multiple measures.
- 7. **Identifying barriers to network modifications**. This technical approach followed in the assessment does not consider potential constraints due to existing policy, monitoring regulations, community concern and other issues. These constraints should be identified to facilitate implementation of assessment findings.

- 8. **Considering additional measures.** Additional measures to consider could include: a trends indicator (e.g., longevity of monitoring record), an emissions weighting factor (e.g., relative density of emissions in vicinity of a monitoring site), a "realtime" (e.g., AIRNow) benefit, and an environmental justice indicator (normalizing income/ property levels).
- 9. **Including cost information**. There should be some quantification of the expected resource savings from shutting down certain monitors to identify reasonable expectations for investing in new monitoring program areas such as air toxics and continuous particulate matter. In addition, the relative "federal" costs contributed to monitoring vary from agency to agency. There is a risk that the assessment will discourage monitoring that is funded by non-traditional sources, such as industry, or through permit fees.
- 10. **Enhancing Information Transfer and Technology.** The utility of monitoring data is enhanced through remote and real time access capability. The Strategy should encourage greater incorporation of automated methods and information transfer. In addition, network design should be strongly linked to AIRNow by enhancing AIRNow's ability to krige monitoring data, and relying on mapping techniques to direct network design.
- 11. **Increasing stakeholder input**. Network assessments and related strategy efforts should solicit advice from the health community (e.g., public schools of health, local and health departments).
- 12. **Encouraging alternative monitoring approaches**. The use of methods, not certified as reference or equivalent, offer enormous data capture potential for relatively low cost. For example, passive ozone monitoring could be used to refine ozone network design and fill in spatial/temporal gaps not provided by existing equivalent methods. Relatively low-cost nephelometers could replace PM<sub>2.5</sub> FRMs in communities desiring monitoring coverage. Mobile approaches could also be used effectively to enhance spatial coverage.
- 13. **Science review**. The national assessment and related strategy should undergo scientific review by CASAC.
- 14. **Transitioning effectively**. It is appropriate to build in sensible transition policies to minimize potential adverse impacts on monitoring agencies and existing infrastructure. This national level assessment has spurred the development and application of several additional network design tools, some of which are discussed in Section 3.4. EPA hosted a workshop in December 2001, dedicated to the application of spatial

analysis tools for network optimization and air quality planning practice. Several of the concerns issued above will be addressed implicitly as the level of application and participation in this field is escalating. During 2002 and 2003, EPA will develop more specific guidance on the use of spatial fields as well as provide expectations with respect to performance specifications.

# 3.3.4 Summary of National Assessment Results

The purpose of this section is to summarize the results of the monitoring network assessment that was conducted as part of the Strategy, and provide general guidance for EPA Regional Offices, States, and interstate groups in conducting their assessments. Three key issues emerged from this assessment:

- 1. Investment Needs: New monitoring efforts are needed to support new air quality challenges, including monitoring for air toxics and new technology for criteria pollutants. Air toxics have emerged as a top public health concern in many parts of the country. Although guidance for deploying a national air toxics monitoring network is still under development, substantial resources appear to be necessary for this monitoring, given the cost to sample for a core set of 18 compounds for 1 year (i.e., about \$60K per site). New technology, especially continuous measurement methods for pollutants, such as fine particles, are needed to provide more complete, reliable, and timely air quality information, and to relieve the burden of manual sampling. Resources and guidance are needed for this activity, as well.
- 2. Divestment Opportunities: To make more efficient use of existing monitoring resources and to help pay for (and justify additional resources for) the new monitoring initiatives noted above, it will be necessary to make certain cuts in the existing monitoring program. Two areas of potential divestment are suggested. First, many historical criteria pollutant monitoring networks have achieved their objective and demonstrate that there are no national (and, in most cases, regional) air quality problems for certain pollutants, including PM10, SO2, NO2, CO, and lead. A substantial reduction in the number of monitors for these pollutants should be considered. As part of this downsizing, it may be desirable to relocate some of these sites to rural locations to provide regional air quality data. Second, there are many monitoring sites with only one (or a few) pollutant(s). To the extent possible, sites should be combined to form multi-pollutant monitoring stations. Any resource savings from such divestments must remain in the monitoring program for identified investment needs. A reasonable period of time must is required to smoothly transition from established to new monitoring activities.
- **3. Importance of Regional Input**: The national analyses are intended to provide broad directional information about potential network changes. Regional/local analyses are a critical complement to the national analyses, and are necessary to

develop specific monitoring site recommendations. To this end, EPA must allow States and regional organizations sufficient time (e.g., at least 6 months) to conduct adequate regional/local analyses.

# 3.4. Regional Assessments and Guidance

As stated earlier, site-specific decisions on network thinning and investments must be conducted with participating agencies. EPA has requested that each Regional Office be responsible for facilitating such assessments and producing preliminary recommendations in November 2002. Attachment 3.2 provides examples of various technical applications and expectations with regard to these assessments.

Attachment 3.3 includes the draft strategy developed by LADCO/Region 5, which has served as a leading example for conducting these assessments. LADCO organized the first regionwide assessment of Region 5 States' air monitoring networks. The process incorporated convening together monitoring and planning functions of the States, and EPA Regional Office staff, and developing objectives and priorities on which to base a range of decisions on investments and divestments. The process benefited from having an NMSC member involved in the meetings as well as periodic input from EPA headquarters. Attachment 3.3 also includes the initial product from this assessment.

# 3.5. Policy Implications

Network assessments produce recommendations on removing or relocating samplers based largely on technical merit. In some instances, these recommendations may be in conflict with existing policy or other needs. For example, a recommendation that an ozone monitor be discontinued in a "nonattainment" county due to redundancy of neighboring sampling sites raises interesting policy/technical issues. Issues such as this need to be resolved following a credible technical recommendation of network realignment. It should not be assumed that policy should override a technical recommendation, nor should technical approach override existing policy. It should be possible to develop case-by-case solutions to these issues where needed. The LADCO/Region 5 monitoring strategy has accelerated this discussion.

#### 3.5.1. Suggestions for Policy/Assessment Conflict Resolution

OAQPS policy and technical staff developed some initial suggestions to address potential conflicts. One example included securing a written agreement between the States and EPA that supplementary data, such as interpolated values, that exhibit acceptable predictive accuracy from neighboring monitoring sites could replace data provided previously by the discontinued site. These suggestions, at this time, do not reflect EPA policy, but signify an attempt to resolve issues in a reasonable time frame. OAPOS intends on developing consistent national level guidance for these topics.

Based on issues which developed as a result of the LADCO/Region 5 assessment, the following represents an initial list of issues and possible solutions:

1) **Issue:** Reluctance to designate some portions of an area nonattainment if it no longer has a monitor that has recorded a violation.

**Possible Solution:** Obtain a written agreement in advance from the agency that is eliminating the monitor that nonattainment/attainment decisions for the county in which the monitor is located will be determined by other specified methods (e.g., modeling or krieging). Where EPA believes there is not sufficient confidence in such methods for the particular situation, the Agency must agree in writing to use another indicator monitor in the area to represent the county (or other regional area) for which the monitor is being eliminated.

2) **Issue:** Reduced number of monitors to apply relative reduction factors (RRFs) for purposes of control strategy development, demonstration of attainment, and evaluation of national measures.

**Possible Solution:** For areas that experience a reduction in monitors, revise EPA guidance on attainment demonstration modeling for the 8-hr ozone NAAQS to apply the RRFs to an interpolated concentration field (e.g., using methods such as krieging based on remaining monitors), rather than to the limited number of remaining monitors. Standardized sets of krieging techniques<sup>2</sup>\* would have to be established, or at least the principles for krieging.

3) **Issue:** Reduced number or monitors to perform model validation.

**Possible Solution:** For areas that experience a reduction in monitors, revise EPA guidance for model validation to allow model validation based on an interpolated concentration field (as in 2 above), rather than on the limited number of remaining monitors. Standardized sets of krieging techniques\* would have to be established or at least principles for krieging.

4) **Issue:** Once an area is designated nonattainment, it may only be designated attainment if it continues to monitor in the area. Deleting a violating monitor may hamper that area's chance of showing that it has attained and may relegate the area permanently to nonattainment.

<sup>&</sup>lt;sup>2</sup>Note that it would take probably a number of years for peer review of these changes in methodology before they could become effective.

**Possible Solution:** Revise EPA policy and procedures for redesignation of an area from nonattainment to attainment to allow the use of an interpolated concentration field (as in 2 above), rather than on a monitor that is eliminated as long as reliance on such methods for the particular area provides sufficient confidence in the results.

In moving forward with the conflict resolution process, the proposed next steps within EPA are as follows:

- Agree on (or modify) the approaches listed above
- Discuss these aspects with modeling groups
- Develop a draft work plan and schedule to proceed
- Brief EPA management on the concepts and work plan and obtain approval to proceed
- Discuss with State and local agencies

Attachment 3.1. National Assessment Figures

Figure 1: 98-00 8-Hour O3 4th Max - Percent of NAAQS: Red=>100%, Purple= 80-100%, Orange= 60-80%, Black= <60%

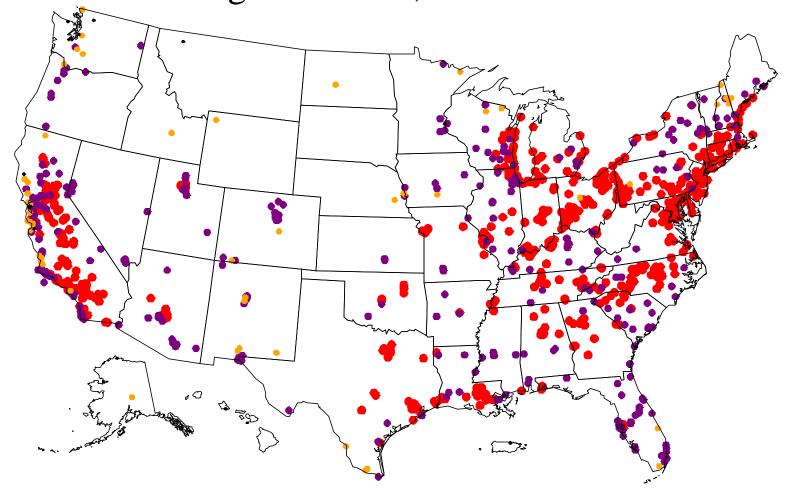


Figure 2: PM25 Annual Mean - Percent of NAAQS: Red=>100%, Purple= 80-100%, Orange= 60-80%, Black= <60%

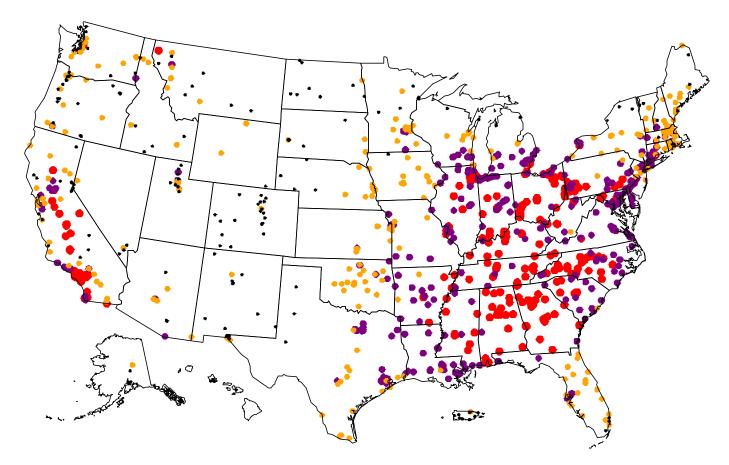


Figure 3: 8-Hour CO 2nd Max - Percent of NAAQS: Red=>100%, Purple= 80-100%, Orange= 60-80%, Black= <60%

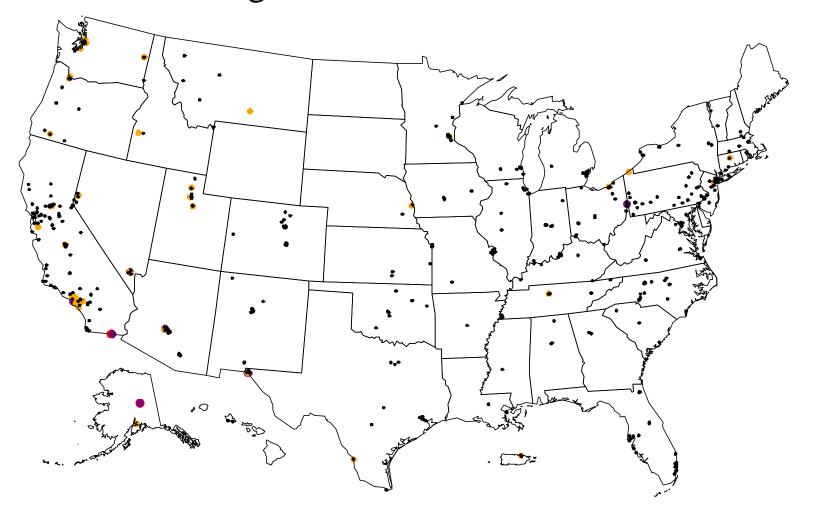


Figure 4: NO2 Annual Mean - Percent of NAAQS: Red= >100%, Purple= 80-100%, Orange= 60-80%, Black= <60%



# Figure 5: SO2 2<sup>nd</sup> Max - Percent of NAAQS:

Red=>100%, Purple=80-100%, Orange=60-80%, Black=<60%

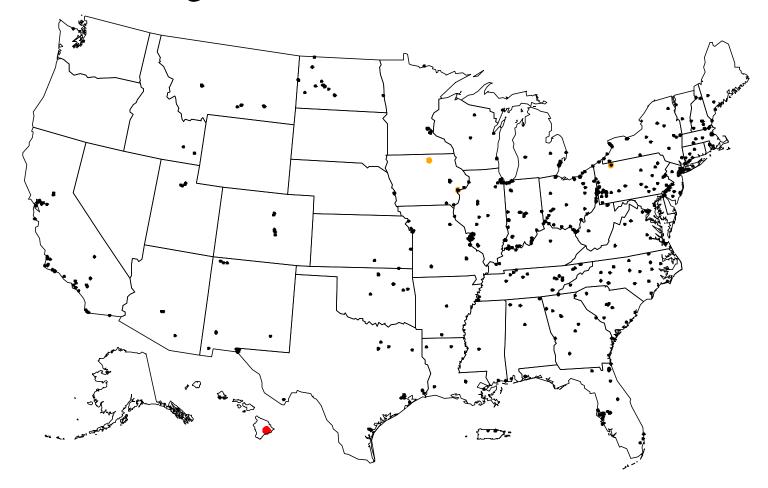


Figure 6: Pb Max Quarterly Average - Percent of NAAQS: Red=>100%, Purple=80-100%, Orange=60-80%, Black=<60%

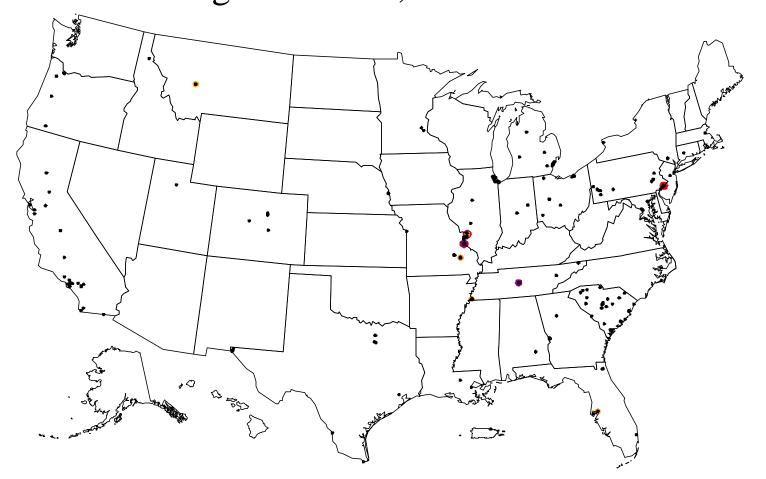


Figure 7: PM10 Annual Mean - Percent of NAAQS: Red=>100%, Purple= 80-100%, Orange= 60-80%, Black= <60%

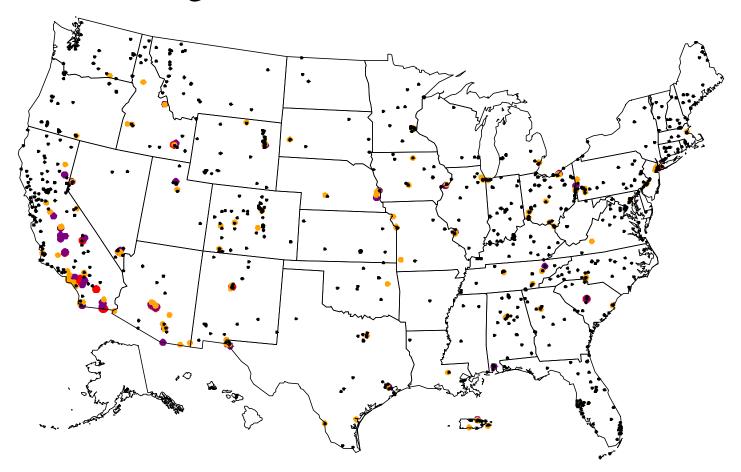


Figure 8: 98-00 1-Hour O3 2nd Max - Percent of NAAQS: Red=>100%, Purple= 80-100%, Orange= 60-80%, Black= <60%

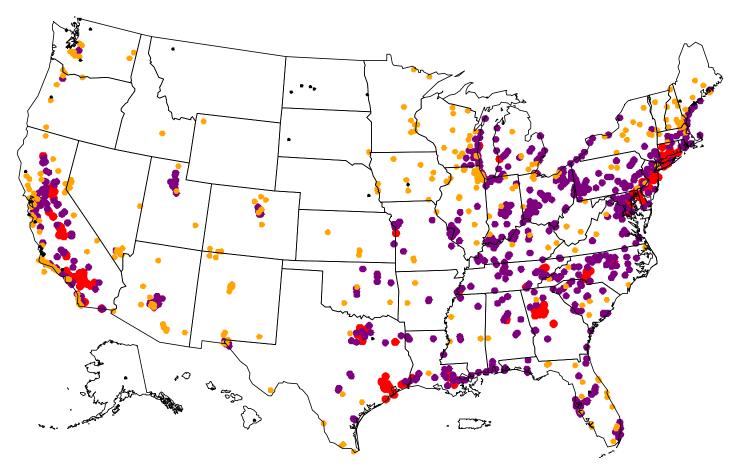


Figure 9: 98-00 8-Hour O3 4th Max - Percent of NAAQS: Red=>100%, Purple= 80-100%, Orange= 60-80%, Black= <60%

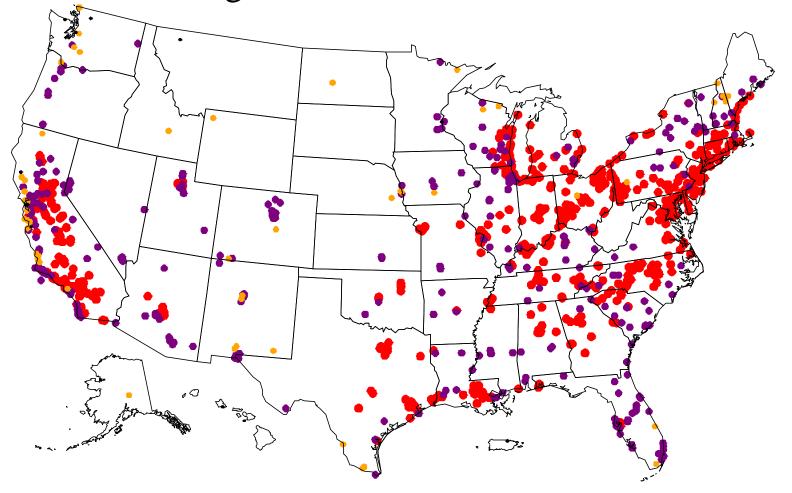
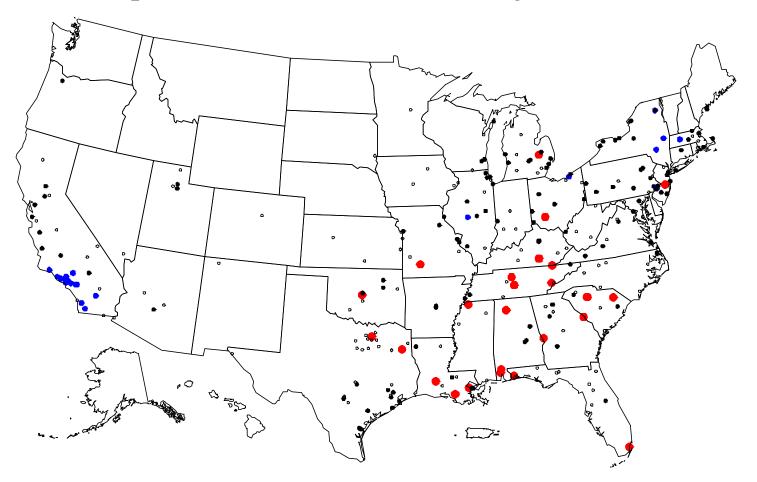


Figure 10: 8-hr O3 10-yr Trends-Aggregate Ranked (Equal Weighting) Sites in 1<sup>st</sup> Quartile (Most Important): Red=Up, Blue=Down, Black=Not Significant



# **Relative Weight of Rankings**

Station Population

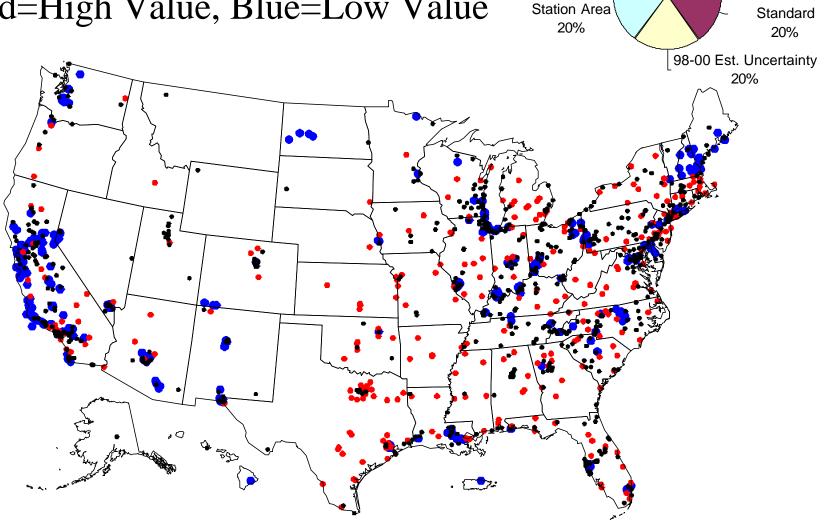
20%

98-00 Concentration

20%

98-00 Value Near

Figure 11: 8-Hour O3 Aggregate Ranking Map: Red=High Value, Blue=Low Value s



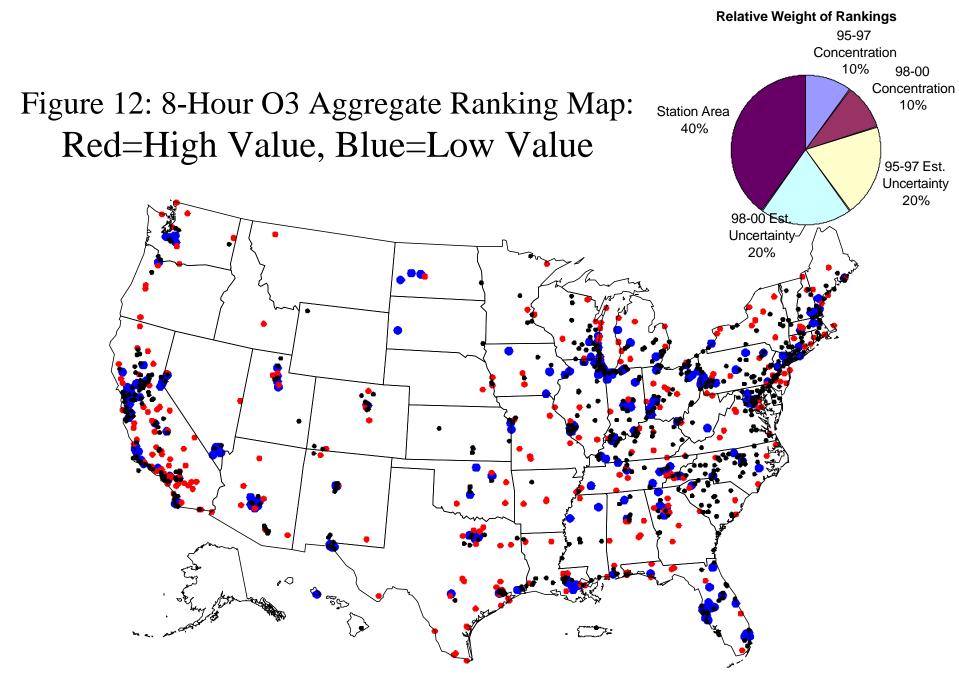
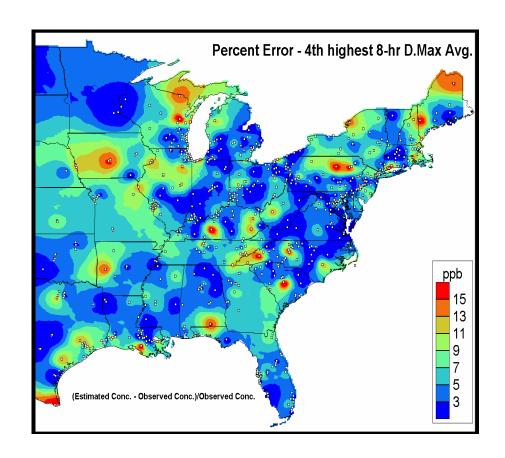


Figure 13: Error mapping for ozone.



# Figure 14: Regional Percent of Sites in National Quartiles

O3 1-Hour Aggregate Data

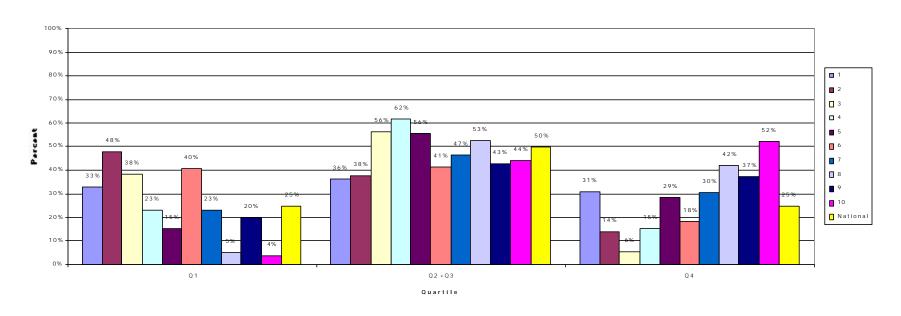
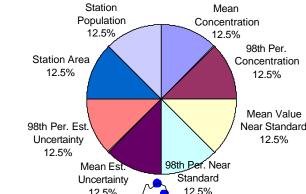
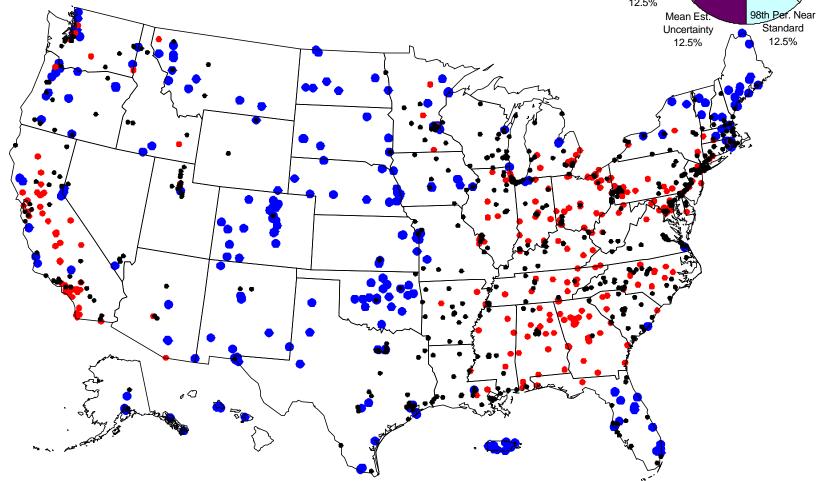


Figure 15: PM25 Aggregate Ranking Map: Red=High Value, Blue=Low Value



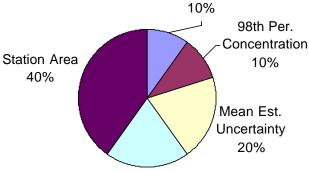
**Relative Weight of Rankings** 

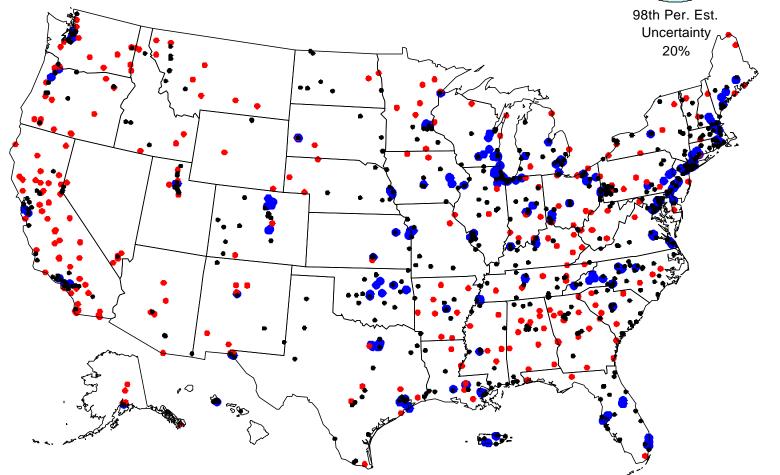


# **Relative Weight of Rankings**

Mean Concentration

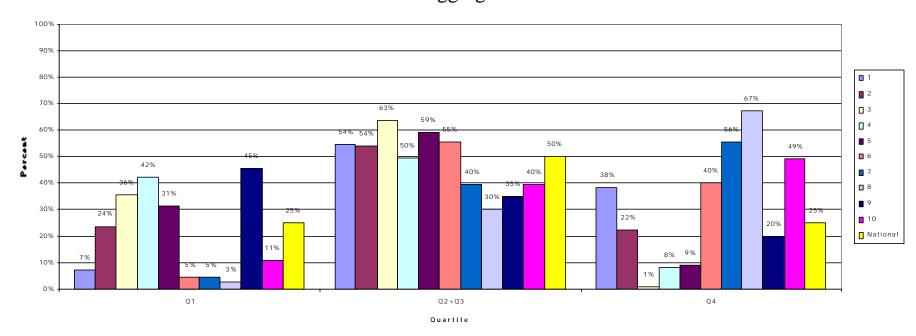
Figure 16: PM25 Aggregate Ranking Map: Red=High Value, Blue=Low Value





# Figure 17: Regional Percent of Sites in National Quartiles

PM25 Aggregate Data



# **Attachment 2: Network Assessment Technical Guidance - DRAFT**

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# I. Goals and Objectives for Conducting Network Assessments

# A. Introduction and Relationship to the National Monitoring Strategy

The EPA and State, local and tribal air monitoring agencies began developing a National Air Monitoring Strategy in 2000 at the urging of EPA. The genesis for the strategy came as a result of concerns about the increasing needs for air quality monitoring data for certain applications, and the pressure of these needs upon the available air monitoring resources. During this same period, the PM2.5 monitoring program deployment was nearing completion and it became evident that monitoring resources had been stretched to their maximum. Complicating this picture was the air toxics program which was looming as another air quality data need that was not being fulfilled. EPA began devoting more effort to examine the existing networks and their supporting mechanisms such as regulations, program priorities, and technologies.

EPA recognizes that some of the regulatory requirements that have remained in 40 CFR 58 for many years should be revised to reflect current program needs. The emission source distributions and levels for certain criteria pollutants, such as sulfur dioxide and carbon monoxide, have changed through the most recent years. The geographic extent of U.S. population growth into sprawling suburbs should also be taken into consideration for those parts of the network that are investigating population exposure types of monitoring. There are many reasons why EPA and its partners in the State, local and tribal agencies must continue to assess and where necessary, modify the air pollution monitoring networks to reflect our changing environment. Network assessments are the key to implementing the national monitoring strategy and to ensuring that the monitoring community uses its resources most effectively.

EPA conducted a national network assessment to start the investigation process. This national-level analysis, while informative in a general sense, was clearly not enough. The concerns of State, local, and tribal agencies could not be adequately taken into account by looking at the program's focus at a national level. This document is an attempt to prepare preliminary technical guidance for the monitoring community on some possible approaches for conducting localized network assessments. This document does not list all possible assessment methods, but it should help begin the process. This document can be expanded as newer tools are developed for this work.

#### **B.** Beginning the Process

Before beginning a review of the various approaches for network assessments, it is important to understand what is considered a network assessment and how this work might vary from what is currently done in the network review process.

The bulk of the *network reviews* that OAQPS has seen include a description of an agency's air monitoring program, specifically, which pollutants are measured in which locations, what changes to sites have taken place over the most recent year(s), what new sites may need to be installed due to new requirements or losing site leases, and how these networks compare against

the national air monitoring regulatory requirements for the criteria pollutants and PAMS requirements. Information on the siting criteria inspections, technical systems audits, and other quality control work is often provided in this annual network review. In some situations, agencies provide information on the size and scope of their network in the form of a printout from the Aerometric Information Retrieval System (AIRS), and in other cases, a report with maps and emissions figures are also included. The network review reporting format varies by Region and even within a Region, with the larger and more sophisticated State and local air monitoring agencies providing more detail on their networks than smaller agencies that may provide a short letter.

EPA's intention is to make the *network assessment* process build upon some elements of the network review by taking a more involved approach that includes reviewing the data collected by the network, discussing data needs with those who are supported by the program, and considering what level of performance can be achieved by the agency. The network assessment may be most effectively illustrated by considering the questions that should be considered.

- -What are the various data collection objectives that a network should meet, at the national and local levels? EPA will revise the existing 40 CFR 58 to make the monitoring regulations more in line with data needs nationally. Regions must also consider what policy decisions must be supported in addition to the technical requirements. An example would include maintenance area monitoring requirements that are part of existing State implementation plans.
- -What air pollutants are being measured and in what locations? Are the "correct" pollutants being measured in the best available locations to meet the national and State/local/tribal data needs? Does the network meet the national regulatory requirements? Are there additional State or local agency requirements that must also be addressed, and does the monitoring system meet these additional requirements?
- -What data needs cannot be met due to limits in my budget/resources? It is important to understand both what can be provided by an ambient air monitoring network, and what cannot based upon existing resources.
- -Are there monitors or sites in the network that would be more effectively located, or should any be removed? There are some arguments that suggest that removing samplers from a site does not save substantial resources. While it is true that the remaining monitors at that site would need to be maintained, removing unnecessary monitors would save on operator time at that site, possibly on the number of quality assurance audits, and on data management and validation.
- -Are any environmental studies taking place in a monitoring agency's area that have a need for the ambient data? How can these additional data interests be supported within available budgets? This support may vary from reconfiguring sites or collection schedules to simply making data available.

-Is the network providing data that are suitable in terms of their quality for the program needs? Are there areas where a monitoring agency needs to improve on performance? Has there been sufficient efforts to conduct technical systems audits, site inspections, and other quality assurance and quality control activities?

-Are there other data sources such as the regional haze program's IMPROVE network, the National Atmospheric Deposition Program (NADP), the Clean Air Status and Trends Network (CASTNet), or special purpose monitoring networks that may be useful to meet the agencies' data needs? Similarly, how does the State, local, and tribal agency network support these programs? Is the monitoring network design in the Region taking full advantage of these other governmental networks?

#### C. Roles, Responsibilities, and Network Assessment Schedules

As discussed briefly in the introduction, localized network assessments must be conducted in order for the network assessment process to be meaningful and achievable. OAQPS expects that each Regional Office will lead efforts among their State, local, and where applicable, tribal air monitoring agencies for network assessments. OAQPS will provide support and guidance when requested; however, the Regions are primarily responsible for the State and local air monitoring stations (SLAMS) networks and for the policy actions that stem from these data.

The Regions may choose to implement their network assessments over their entire geographic region by working with their monitoring agencies as a group, or individually. If the latter approach is taken, it is important that the Region consider monitoring in adjacent States or local areas that may produce data that are useful for informing a more localized assessment or data need. Both ozone and fine particles appear to drive many of the regulatory data needs; therefore, it makes technical sense that a regional approach is reasonable. OAQPS recognizes that many other factors will contribute to a Region's decision on how to most appropriately conduct their network assessments, and offers flexibility to the Regions in making this decision.

OAQPS requests that initial network assessments for the entire country be completed this year to start the process. <u>Initial network assessment drafts should be provided by October 2002 from each Region to OAQPS.</u> EPA does not expect that these initial draft assessments will have undergone the needed consensus building process by October; however, it is important that some effort take place this year. OAQPS expects that between October 2002 and February 2003 that Regions, States, locals, and tribal agencies will refine these initial draft assessments and complete a final network assessment by March 2003. These final network assessments should consider the technical data needs, some of the logistical requirements for making the network changes, policy implications for any network changes, and of course, resource implications for making identified changes. Full consideration for how network changes may be realized will occur throughout 2003 as the networks are modified.

The OAQPS will review both the draft and final network assessments for national consistency issues in November 2002 and April 2003, respectively. OAQPS does not expect that each Region or monitoring agency will take necessarily the same approach toward conducting

network assessments. There are a variety of approaches that could be foreseen that are equally valid. The OAQPS review will focus on the end results of these assessments and how they answer the questions listed above.

As for ongoing network assessments, OAQPS suggests a 5-year cycle for full network assessments. As with the initial assessments, the Region may choose to conduct these assessments at one time for the entire Region, or on a rotational basis. Conducting full network assessments annually is too large a burden, and not truly appropriate given that our NAAQS are generally multi-year standards that require multiple years of data at individual sites. OAQPS also recognizes that emission changes due to increasing controls are not likely to occur in a single year, and revisiting the networks over a longer period is warranted.

OAQPS intends to propose in upcoming regulatory changes that network assessments be added as a requirement. It will be important to also update language on annual reporting and certifications to reduce burden in these areas and to make better use of newer data management systems that eliminate the need for lengthly certification reports. OAQPS also proposes that deviations from national monitoring requirements are allowed for those agencies that participate in conducting an appropriate and approved network assessment that demonstrates that their alternative network meets the national needs as well as their own local needs.

#### II. Technical Tools

Regions and States can use any technically appropriate analytic tool or technique for their network assessments. They are encouraged to use multiple approaches. Similar results from different techniques can strengthen a case for reduced or redistributed monitoring, however, contrasting results may also be illuminating. Different approaches may yield different results because each approach probably has a slightly different objective/goal. Studying the different approaches and results will lead to a greater understanding of the various objectives and therefore lead to a network assessment most appropriate for the Region and/or State.

Several recently applied network assessment techniques, including the 'National Assessment' approach and various Regional methods, are described below. Some techniques and tools still under development are also noted. The intent of this list is not to provide all the details, rather to provide overview and motivation for the various techniques. Web links and/or contact information are provided in order for interested parties to obtain additional information. This is not an exhaustive list of methods. Also, the techniques listed below are provided for reference only. Regions / States can use these techniques, however, some may not be applicable to all areas or networks. Whatever techniques/tools are used, there should be a clear connection between the analytic results and the proposed network changes. Periodic updates to this document will highlight progress with the evolving methods and document additional illustrative Regional efforts.

# A. National Assessment:

A National assessment of the criteria monitoring networks was completed in June 2001. The assessment consisted of three distinct parts: 1) an evaluation of measured concentrations as a percentage of the NAAQS, 2) a multi objective 'information value' ranking scheme which shows the relative value of each monitor according to different monitoring objectives, and 3) a trends evaluation. These pieces are described in broad terms below. The full analyses, including details of the technique, can be found at <a href="http://www.epa.gov/ttn/amtic/netamap.html">http://www.epa.gov/ttn/amtic/netamap.html</a>. Although the National assessment was purposefully very general and did not advocate specific network cuts / changes, the approaches utilized may be appropriate for more refined, local assessments of the monitoring networks which can lead to actual network changes.

# National Assessment components:

- 1. Evaluation of measured concentrations as a percentage of the NAAQS: An annual metric, corresponding to each criteria pollutant NAAQS, was computed for every active monitor for years 1998, 1999, and 2000. A 3-year average ('design value') of this metric was then calculated. [Note: Since PM<sub>2.5</sub> monitoring did not begin in earnest until 1999, a 2-yr 'design value' was used for the 2 PM<sub>2.5</sub> NAAQS metrics.] The 'design values' were compared to the NAAQS levels and assigned one of 4 bins: 100% or more of NAAQS, 80-100% of NAAQS, 60-80% of NAAQS, and less than 60% of NAAQS. Results were mapped and a National aggregation was bar-charted. Sites in the lower two categories, especially those 'less than 60% of NAAQS' have limited value for NAAQS usage. Although NAAQS usage is one of the central objectives of the criteria networks, other uses and objectives also exist and should be considered. The next described component of the National analyses considers multiple objectives.
- 2. Multi-objective 'information value' ranking scheme: Five independent measures were chosen to represent the information needs for population exposure, compliance monitoring, and tracking / model evaluation. These measures are: concentration, uncertainty (in 'design value'), deviation from NAAQS, area represented, and population represented. Each monitor was ranked (by pollutant / metric) according to those five measures. The 3-year 'design values' (computed as described above) were used in the calculations of the first three measures. A monitor's location relative to other monitors in the network was used to derive a 'sampling zone' polygon; these polygons were used to compute the latter two measures. Maps were produced for each of the five measures; the monitors in the highest ranked quartile were coded red, the monitors in the middle quartiles were coded black, and the monitors in the bottom quartile were coded blue. Hence, the red monitors were the most important (for that measure) and the blue monitors were the least important. The measure rankings were then aggregated based on several different weighting schemes and composite maps produced (using the same color scheme). Ancillary outputs such as 'Regional Breakdowns of the National

Quartiles' and 'Tables of Quartile cutoffs (in measure units)' were also produced.

3. Trends evaluation: A non-parametric 'trend' routine (the same one used in the annual Trends reports) was applied to each monitor's annual metrics in 5- and 10-year cuts ('96-'00 & '91-'00). Each monitor was assigned one of 4 categories: significant upward trend, significant downward trend, no significant trend, or insufficient data. Results were summarized in pie charts. For a case study, the monitor trend information was merged with the output from #2 above and new maps produced showing the trend for specific quartiles (e.g., the blue category) of the aggregate 5-measure ranking. The rationale for this output was, even if a site is 'low value' (blue) in aggregate measure maps, you may want to keep the monitor if it has an upward trend.

Contact: Mark Schmidt (EPA-RTP, OAQPS): (919) 541-2416

# B. <u>LADCO/Region 5 Approach:</u>

LADCO organized the first regional wide assessment of Region 5 States air monitoring networks. The assessment effort serves as a model for other regions throughout the country. The major process incorporated convening together monitoring and planning functions of the States, and EPA regional office staff, and developing objectives and priorities on which to base a range of decisions on investmets and divestments. The process benefitted from having an NMSC member, Mike Koerber, involved in the meetings as well as periodic input form EPA headquarters. Attachment 3 includes the initial product from this assessment.

In response to the ozone and  $PM_{2.5}$  networks submitted to the Region by their monitoring agencies, the EPA Region 5 Air Monitoring Section reviewed the networks using a variety of data analysis techniques to determine the importance of monitoring sites. The Region 5 assessments of their ozone and  $PM_{2.5}$  networks are capsuled below:

# Ozone Assessment in Region 5:

#### Summary and Introduction

Region 5 analyzed the 1996 through 2000 daily 8-hour maximum ozone concentrations measured within the Region as well as surrounding areas to assess the current condition of the individual monitoring sites in relation to each other. The expected outcome of this analysis is a decision between the Region and the State and local air monitoring agencies as to which monitoring locations could possibly be terminated, relocated, or established. To meet this objective, several analyses were conducted. The primary analyses focused on examining how relationships and concentration ratios between monitors are affected spatially between sites. The results of this analysis are intended to complement those obtained through the National Network Assessment.

#### Data

Hourly ozone concentrations were polled from the U.S.EPA Aerometric Information Retrieval System (AIRS) for the years of 1996 through 2000. Only data collected during the primary ozone forming months (May through September) were used for the geographic area of interest. Daily maximum 8-hour averages were calculated as prescribed in 40 CFR Part 50 Appendix H for each of the monitoring sites used in the analysis. All data regardless of flags in AIRS were included.

<sup>&</sup>lt;sup>1</sup>Tribal air monitoring activities in the Region 5 area are just beginning to be implemented, and modifications or reductions to their networks are not expected at this time. Tribal agencies will want to use these tools in future assessments after their programs have been developed.

#### Analyses

# Ozone Correlograms

Pearson correlation coefficients (r) were calculated using SAS for every possible monitoring pair combination. A valid correlation coefficient was defined as one where there were at least 75 data points from each of the monitor pairs. Distances between sites were calculated using the following formula:

```
\label{eq:cos} \begin{split} & \text{distance} = \arccos[\cos(\text{lat1})*\cos(\text{lon1})*\cos(\text{lat2})*\cos(\text{lon2}) + \\ & \cos(\text{lat1})*\sin(\text{lon1})*\cos(\text{lat2})*\sin(\text{lon2}) + \sin(\text{lat1})*\sin(\text{lat2})]*3963.1925 \text{ miles} \\ & *1.609344 \text{ miles/km} \end{split}
```

where: lat1 and lon1 are the latitude and longitude coordinates of monitor one, lat2 and lon2 are the latitude and longitude coordinates of monitor two, 1.609344 miles/km is the conversion factor of miles to kilometers.

Plots of the correlation between the two sites and their respective distances were created for every Air Quality Control Region (AQCR) in the Region 5 area of interest. In general, the correlation between two monitors diminishes as the distance between the monitors increases. These plots mainly were used to determine if there were any monitors which were relatively close to each another and had a relatively low correlation between their ozone measurements. This would signify that the monitor pair may be measuring concentrations unique to each site.

# Plots of Correlation vs. Ratio between 2 monitors

Ratios of the concentrations between the monitor pairs used in the Correlogram analysis were calculated. Plots of the correlation of the two sites versus the ratio of the two sites were created to help determine if any highly correlated sites had significantly different concentrations.

# Plots of Ratio vs. Distance between 2 monitors

Plots were created that display the ratios from the previous analysis versus the distances from the correlogram analysis. This analysis expands on the two previously described procedures to determine sites which are close to each another and may or may not have similar ozone measurements.

# **Summary Tables**

Tables such as the excerpt below summarize the results from the Correlogram, Correlation vs. Ratio, and Ratio vs. Distance analyses.

Site 1	Site 2	Distance (km)	No. Obs.	Corr: R	Avg. Ratio	Median Ratio	Std. Dev.	Min. Ratio	Max. Ratio
		/	Obs.	К	Rano	Kano	Dev.	Ratio	Kano
17031000144201	17031003244201	18.2	759	0.81	0.86	0.89	0.22	0.16	2.07
1	1								
17031000144201	17031003744201	34.7	92	0.83	1.14	1.12	0.33	0.21	2.67
1	1								
17031003244201 1	17031006344201	15.4	747	0.69	1.97	1.71	0.95	0.75	9.25

# **PMF** Results

Positive Matrix Factorization (PMF) was used to determine clusters of monitors displaying similar characteristics based on the concentrations measured at each site. PMF is an analysis technique similar to ordinary factor analysis except that it iteratively solves for both the factor loadings and scores and then predicts an individual monitor concentration. [See <a href="ftp://rock.helsinki.fi/pub/misc/pmf/">ftp://rock.helsinki.fi/pub/misc/pmf/</a> for details on PMF.] The factor loadings allow for the identification of groups of monitoring locations which exhibit related ozone concentrations. For this, 8-hour daily maximum ozone concentrations were used. Since this analysis requires a complete data record, missing days were estimated using a linear interpolation. Sites which had large amounts of data missing were removed from the analysis entirely.

# PM<sub>2.5</sub> assessment in Region 5:

#### **Summary**

The purpose of this evaluation was to help the Region 5 monitoring agencies to assess the relative value of existing PM<sub>2.5</sub> monitors. This effort addresses the second basic objective identified in the *Regional Strategy* - identification of divestment opportunities. Parallel efforts by Region 5 and their monitoring agencies will identify areas for potential addition of PM<sub>2.5</sub> and other criteria pollutant monitors and will also promote expansion of the *State and Local Agency Regional Air Toxics Monitoring Network*.

#### *Analyses*

The Region 5  $PM_{2.5}$  monitors were evaluated on the basis of four decision criteria: 1) mean concentration, 2) monitor density, 3) correlation, and 4) population change. These criteria were designed to provide insight into the relative value of monitoring sites on the regional scale. The four criteria are described below and general findings are presented. This section is followed by suggestions on how to apply these findings.

## Mean Concentration

A mean concentration and standard deviation were calculated for each monitor for the period of January 1999 - March 2001. Results were compiled in a spreadsheet and also mapped.

Sites with fewer than 60 measurements were not evaluated (coded 'NA' on the spreadsheet). Sites were color-coded on maps and spreadsheets to indicate their relative value in terms of  $PM_{2.5}$  concentration. Region 5 monitoring sites were divided into five equally sized groups (quintiles) and color-coded as follows:

blue	$6.86 - 12.21 \mu\text{g/m}^3$ (lowest value sites)
light blue	12.24 - 14.04 μg/m³
pink	$14.05 - 15.33 \mu g/m^3$
red	$15.34 - 17.32 \mu \text{g/m}^3$
dark red	$17.34 - 20.82 \mu\text{g/m}^3$ (highest value sites)

Please note that the same quintile color coding was used throughout the entire analyses. Monitors measuring lower  $PM_{2.5}$  concentrations (with respect to the quintile ranges) are deemed less valuable than those giving higher measurements.

# Site Density

Distance was measured from each individual monitor to the next nearest site, not including co-located monitors. Monitors in adjoining Regions were also considered as potential closest sites. Sites are color-coded on maps and spreadsheets to indicate their relative value in terms of site density. Monitors located closest to another site are deemed less valuable than those more isolated from other sites. Sites were divided into quintiles with blue sites having the lowest values (distance to nearest PM<sub>2.5</sub> site) and dark red sites having the furthest distances.

#### **Monitor Correlation**

Pearson correlation coefficients (R) were determined for each pair of monitors in Region 5 and adjoining states. The single highest correlation coefficient (R) for each monitor was identified. Results were compiled in a spreadsheet and also mapped. Sites with fewer than 60 measurements were not evaluated (coded 'NA' on the spreadsheet). Sites were color-coded on maps and spreadsheets to indicate their relative value in terms of monitor correlation. Monitors most highly correlated to another site are deemed less valuable than those with lower correlations. Dark red sites have the lowest R values and blue sites have the lowest R values.

#### Population Change

Percent population change (between 1990-1999) was indicated for the county in which each monitor is located. Data were obtained from the U.S. Census Bureau.

## Application of Network Assessment Results

The above described decision criteria are not intended to be used independently, that is, we should not simply eliminate all low-reading monitors or cut the most highly correlated monitors in the Region. Rather these criteria should be considered together and incorporated with other factors specific to each State and local agency. Despite the fact that the four decision

criteria are quantitative in nature, it is difficult to quantitatively evaluate a group of monitors considering all four criteria simultaneously. The network reviewer may either: a) look at all decision criteria simultaneously in a qualitative way, or b) look at the criteria quantitatively in a stepwise manner as described below.

The following steps may be followed to identify the best candidates for elimination from a network. The network evaluator must first prioritize the importance of the described decision criteria. The suggested steps assume the following prioritization in decision making (criteria listed in decreasing order of importance): a) density, b) correlation, c) mean, d) population change.

- 1. Locate the information pertaining to the metropolitan area or State of interest on the results spreadsheet. Copy the pertinent rows into a blank spreadsheet.
- 2. Sort the rows based on Site Density.
- 3. Narrow the list by deleting the 50% of sites with the highest monitor value for Site Density, i.e., monitors which have a farther distance to the next monitor
- 4. Sort the remaining rows based on Correlation
- 5. Further narrow the list by deleting the 50% of sites with the lowest value for Correlation, i.e., monitors with lower correlations
- 6. From these remaining sites (the most redundant 25%), consider those with lower concentration means and lower population growth as the first candidates for network elimination.
- 7. Incorporate local issues and priorities in making final decisions

An alternate prioritization of the four criteria is possible, for example correlation may be considered the most important factor to consider, rather than site density. Further, the network reviewer may narrow the list to a different extent (more or less than a 50% cut in steps 3 and 5) depending on the size of the current network, the number of desired deletions, or other considerations. It is up to the monitoring agencies to decide how to best apply these results. According to the described assumptions, the sites remaining in the table may be considered the leading candidates for elimination in the Region. A portion of the table from the Region 5 analysis is shown below.

AIRS ID	Mean (μg/m³)	Distance to	Correlation,	County
		Next Site	Highest (R)	Population
1716100031	14.84	6.4	0.966	-15 to 0%
5507900592	14.54	6.9	0.971	-15 to 0%
5507900991	14.45	2.0	0.978	-15 to 0%

Agencies may wish to follow this same process on a statewide or citywide level to determine relative value of monitors on their localized scale. If multiple sites from the same area are left in the table, the reviewer should not assume that all should be eliminated! Rather, the State should select <u>among</u> these sites, with the prime candidates identified as the monitors with a combination of lowest mean, highest density, and highest correlations. States may need to cycle

through the entire process (including recomputation of the 4 metrics) after 'eliminating' a single or small number of monitors since the metrics and relative site values may change.

Contacts: Motria Poshyvanyk (EPA Region V, ARD): (312) 886-0267 [PM<sub>2.5</sub>]

Mike Rizzo (EPA Region V, ARD): (312) 353-6324 [ozone]

## C. Region 3 Approach

The approach to network assessment being proposed by Region III includes both the use of spatial fields and a decision making procedure (Multi-criteria Integrated Resource Assessment MIRA), developed in the Region, that allows for the simultaneous consideration of all relevant and quantifiable criteria. The approach is based upon a premise that tries to define air quality as an estimated spatial field of concentrations with a corresponding estimated field of uncertainties. The geostatistical technique of kriging is used to estimate air quality fields. The scientific merit of a given network design is judged on the certainty with which the actual concentration field can be reproduced from its measured data. The uncertainty field is constructed using modeled benchmark fields of concentrations that present a rational representation of possible future air quality, that is, air quality fields that the designed network is likely to encounter. The MIRA procedure was designed to help make informed and inclusive environmental decisions. It is a modular approach consisting of a Modular Data Collection Manager (DCM) which organizes, warehouses, and prepares data for analysis; a Geostatistical Indicators Module (GIM) that creates environmental indicators (reducing spatial maps to single indexed values for use as indicators); and a Decision Analysis Module which brings data, indicators, judgments together for holistic decision making. The general procedure Region 3 intends to use for network assessment is as follows:

- 1. Develop an appropriate set of modeled benchmark spatial fields.
- 2. Construct potential new network designs.
- 3. Construct a subset of concentrations from the benchmark fields based on the locations of the proposed monitoring sites.
- 4. Krig the concentration subsets producing an estimate of the benchmark field.
- 5. Construct an uncertainty field by comparing the benchmark to the estimated benchmark fields.
- 6. Establish decision criteria.
- 7. Quantify the criteria for each network design.
- 8. Apply the MIRA decision approach.

#### Additional References:

C Air Quality Data: A New Conceptual Approach
<a href="http://www.epa.gov/ttn/amtic/files/ambient/pm25/workshop/spatial/cimorelli.pdf">http://www.epa.gov/ttn/amtic/files/ambient/pm25/workshop/spatial/cimorelli.pdf</a>

Contacts: Alice Chow (EPA Region III, AP): (215) 814-2144 [MIRA]

Al Cimorelli (EPA Region III, APD): (215) 814-2189 [spatial fields] Cynthia Stahl (EPA Region III, APD): (215) 814-2180 [MIRA].

## D. <u>Design Interface Tool</u>

The Design Interface (DI) is a software package that provides a graphical interface to evaluate alternative networks. The Design Interface makes extensive use of S-Plus which is a software package widely used by statisticians and data analysts. The existing version of DI allows users to input an arbitrary network of ambient monitors along with mathematical formulas used to describe the spatial structure of the data. From this information, the user is able to delete or add monitoring stations and display the consequences in terms of spatial predictions and uncertainties. For example, users can estimate the probability that an unmonitored area is exceeding a harmful threshold given concentration data from the network of nearby monitoring stations. Software and documentation for the current version of DI is available at the following web site: http://www.cgd.ucar.edu/stats/DI/.

EPA is upgrading DI to improve the data interface to DI so that data from AIRS and other sources can be easily inputted into the system. In addition, DI is being modified to include technical improvements and flexibility for the user in selecting network performance measures needed to evaluate alternative monitoring network designs. A feature will be added to enable users to examine and validate statistical assumptions about the spatial covariance structure and permit simple graphical display of correlation among monitors using brushing and highlighting techniques. Documentation will be significantly improved and example problems expanded to include ozone and PM<sub>2.5</sub> for a hypothetical planning area. Since DI is structured around the S-Plus language, users of DI must have access to S-Plus and the S-Plus spatial module. The enhanced version of DI should be available for user testing by late spring 2002.

Contact: Bill Cox (EPA-RTP, OAQPS): (919) 541-5563

## E. Additional Techniques Under Development

The elements listed below came to fruition based on discussions at the Spatial Data Analysis Technical Exchange Workshop held December 3-5, 2001 in the Research Triangle Park, NC. [Presentation materials from that workshop can be found at <a href="http://www.epa.gov/ttn/amtic/spatlwrks.html">http://www.epa.gov/ttn/amtic/spatlwrks.html</a>.] The activities listed below will be pursued in parallel with each of the ongoing monitoring network assessments. The purpose of these elements is to establish a framework for generating reliable spatial fields. The statistical theory that is used to develop space-time models of ambient concentrations is evolving. As techniques and tools are developed, these will be made available for use in understanding airsheds, designing monitoring networks, developing control strategies, and supporting epidemiological studies.

One element is a white paper, proposed to be completed in April 2002. At the workshop, several people suggested that the participating scientists prepare a white paper describing the benefits of using interpolated spatial fields instead of using only points in space. There are several statistical papers addressing this approach. Summaries of these papers together with a discussion about the potential policy uses of spatial fields will comprise the white paper. The workshop participants agreed that this white paper could be a catalyst for getting spatial fields into the regulatory process.

The second element is a round robin by collaborators and EPA scientists to compare and contrast various techniques for developing fields of spatial predictions and associated uncertainties. Three to five emerging techniques as well as some of the techniques described in this Guidance will be part of the round robin, and each technique will be applied to the same database. The basics of the round robin include a series of objectives that get progressively harder. What is learned from each stage will hopefully be incorporated into existing tools, such as the previously mentioned Design Interface tool, so that agencies can use the tools for improved spatial prediction and network design. The series of objectives include:

- 1. Prediction of field of PM<sub>2.5</sub> 3-year average of annual average concentrations and uncertainties.
- 2. Prediction of field of PM<sub>2.5</sub> 3-year average of 98<sup>th</sup> percentiles and uncertainties.
- 3. Forecasting of field of daily PM<sub>2.5</sub> concentrations in support of public reporting.
- 4. Prediction of 3-year average of 4<sup>th</sup> max 8-hour average ozone concentration.
- 5. Multi-pollutant prediction.
- 6. Optimal designs.

Contacts: Shelly Eberly (EPA-RTP, OAQPS): (919) 541-4128 Ellen Baldridge (EPA-RTP, OAQPS): (919) 541-5684

## III. Acronyms & Web Sites

AIRS - U.S. EPA's Aerometric Information Retrieval System (reference web site: <a href="http://www.epa.gov/airsdata.">http://www.epa.gov/airsdata.</a>

AQCR - Air quality control region (reference 40 CFR 81)

CASTNet - Clean Air Status and Trends Network (reference web site: <a href="http://www.epa.gov/castnet">http://www.epa.gov/castnet</a>)

CFR - Code of Federal Regulations

DCM - Data collection manager

DI - Design interface tool (reference web site: http://www.cgd.ucar.edu/stats/DI/)

GIM - Geostatistical indicators module

IMPROVE - Interagency Monitoring of Protected Visual Environments (reference web site: http://vista.cira.colostate.edu/improve)

MIRA - Multi-criteria integrated resource assessment, developed by EPA Region 3.

NAAQS - National Ambient Air Quality Standards (reference 40 CFR 50)

NADP - National Atmospheric Deposition Program (reference web site: <a href="http://nadp.sws.uiuc.edu">http://nadp.sws.uiuc.edu</a>)

NMSC - National Monitoring Strategy Committee (reference web site: http://www.epa.gov/ttn/amtic)

OAQPS - Office of Air Quality Planning and Standards, U.S. EPA

PMF - Positive matrix factorization (reference web site: <a href="ftp://rock.helsinki.fi/pub/misc/pmf/">ftp://rock.helsinki.fi/pub/misc/pmf/</a>)

QA - Quality assurance

RTP - Research Triangle Park, North Carolina

SLAMS - State and local air monitoring stations (reference 40 CFR 58)

## Attachment 3.3

# **Draft LADCO/Region 5 Air Monitoring strategy**

## REGIONAL MONITORING STRATEGY

The purpose of this document is to propose a strategy on how to best utilize available resources for ambient monitoring in the Region V States. The strategy reflects two basic objectives:

- (1) Investment Needs: New monitoring efforts are needed to support new air quality challenges, including monitoring for air toxics and new technology for criteria pollutants.
- Divestment Opportunities: To make more efficient use of existing monitoring resources and to help pay for (and justify additional resources for) the new monitoring efforts, it will be necessary to make certain "cuts" in the existing criteria pollutant monitoring networks. A fundamental assumption in this strategy is that any resource savings resulting from these cuts in a given state will be reinvested to support additional monitoring efforts within that state.

It is expected that this document will need further review and discussion within each state and with the general public before it can be finalized.

#### I. CORE PRINCIPLES

The regional monitoring strategy was developed consistent with the following core principles:

- State-by-state recommendations to improve (decrease, increase, relocate, revise) existing criteria pollutant monitoring networks based on consideration of:
  - i. public information<sup>1</sup>
  - ii. public health/compliance with NAAQS
  - iii. strategy development (i.e., support modeling)
  - iv. trends/strategy evaluation
  - v. multi-pollutant sites (supersites)
  - vi. regional-scale (O3, PM2.5) v. local-scale (CO, SO2, Pb, PM10) pollution problems
  - vii. population-oriented sites
  - viii. over-monitoring (redundancy) and under-monitoring
  - ix. low concentrations
  - x. state rules
  - xi. population growth

<sup>&</sup>lt;sup>1</sup> The states are committed to providing the public with air quality data on a near real-time basis. To this end, each state has established a web site where daily ozone data are available and has participated in USEPA's ozone mapping project, as part of EMPACT. These efforts, especially EMPACT, have been very successful. Unfortunately, USEPA will be discontinuing funding for EMPACT before the program can be expanded to deal with other air pollutants which may pose as much of a threat to public health as ozone. For example, at some locations in the Region V States, there were more days in recent years in the "unhealthy for sensitivity groups" category for PM2.5 than O3. It is, therefore, recommended that USEPA continue funding EMPACT to ensure that it will provide the public with near real-time information for all air pollutants, as appropriate.

- Establish regional air toxics monitoring network
- Not bound by Federal regulations and policies; need to change NAMS/SLAMS regulations and nonattainment policies
- Evaluate new technology
- Provide for state/local flexibility (address local needs e.g., TSP in WI)
- Ensure adequate data quality assessments, including regionally consistent procedures for quality assurance, data validation, and data interpretation
- Address important administrative issues, including public outreach, reinvesting resource savings, preserve funding and jobs (with retraining opportunities), and a general understanding of the long-term direction of the national program
- II. RECOMMENCED CRITERIA POLLUTANT MONITORING CHANGES
  Based on the core principles outlined above, each state reviewed their existing
  criteria pollutant monitoring networks and identified proposed changes to be
  phased-in over the next two to three years. The proposed changes are
  summarized in Table 1 and Figures 1 7. In general, these changes reflect
  elimination of several existing monitors, establishment of a few new monitors, and
  a movement toward multi-pollutant sites. The number of monitoring sites in each
  state (including industrial monitors in IN and WI) before and after these proposed
  changes are as follows:

	O3	PM2.5 Mass	PM2.5 Cont	PM2.5 Spec	PM10	TSP	Pb	CO	SO2	NO2
IL	42/33	35/32	2/2	6/6	17/11		15/7	9/8	22/19	10/9
IN IN-ind.	43/35 2/1	40/30	3/3	2/7	25/22 11/5		6/6 3/2	5/4 0/1	8/7 28/27	4/4 2/0
MI	25/15	27/18	10/10	9/10	9/2		10/6	7/5	7/5	4/4
MN	7/7	22/17	1/3	1/3	19/13		2/2	10/10	8/8	4/4
ОН	51/40	48/46	2/2	14/14	72/33		14/5	15/10	32/19	4/3
WI WI-ind.	36/30	28/22	3/3	6/6	6/6	15/15 16/16	0/0	5/2	4/3	4/4
Total	204/160	200/165	21/23	38/46	148/87	15/15	47/26	51/39	81/61	30/28

(Note: numbers above reflect number of sites "before" / "after")

Several comments on the proposed changes should be noted:

- Only minor reductions in the existing ozone networks are proposed. This is appropriate given the current widespread 8-hour ozone problem in the region. Some of the proposed changes involve relocation of monitors to rural areas to provide information on regional ozone levels.
- Only minor reductions in the existing PM2.5 FRM networks are proposed at this time. It is believed that three full calendar years of data are needed for NAAQS compliance determinations before any massive reductions are considered. It is, however, reasonable to consider at this time: (1) relaxations in the sampling frequency to 1-in-6 day at sites where the annual NAAQS is clearly controlling, and (2) elimination of low concentration, redundant FRM monitors if resources are needed now to support deployment of speciation or continuous monitors. Once three full years of data are collected, then divestment in FRMs and investment of continuous monitors should be pursued. Guidance and support is needed from EPA on moving from filter-based to continuous measurements.
- Significant reductions in PM10, Pb, CO, SO2, and NO2 networks are proposed, consistent with the absence of any regional air quality problems for these pollutants. Further reductions in the number of monitors will be considered.
- A preliminary cost analysis was performed to determine the cost savings associated with the proposed reductions. For example, it is estimated that the shutdown of 27 parameters at 22 sites in Illinois would save about \$275K. Based on these approximate costs and the proposed reductions in the other states, the savings appear range from less than \$100K in Minnesota to more than \$500K in Ohio. While not insignificant, these savings will not be sufficient to pay for new monitoring efforts, such as a regional air toxics network.
- Several graphical analyses performed by USEPA, Region V are supportive of the proposed changes. These analyses include correlation maps for ozone and PM2.5, PMF analysis, and krieging analysis (see Figure 8). In particular, these analyses demonstrate redundancy in the existing ozone and PM2.5 monitoring networks.
- An additional review of the proposed changes should be conducted to address
  the adequacy of the regional/rural monitoring coverage, and to identify any
  additional opportunities for combining sites (i.e., supersites). Note, several of
  these supersites appear to qualify as "national core" (NCORE) sites, which are
  being considered in draft USEPA guidance:
  - o IL Northbrook and E. St. Louis
  - o IN Gary (IITRI) and Evansville (F.S. #17)
  - o MI Detroit (E. 7 Mile), Grand Rapids, and Seney
  - o MN –
  - o OH Cleveland (14th St.), Cincinnati (Taft Rd), and Steubenville
  - o WI Milwaukee (SER Hdgs) and Mayville

 In addition to the criteria pollutant monitoring, it should be noted that the States support several other related monitoring programs. These programs include the base 9-station PAMS network:

Туре	Purpose	Site
1	background	Braidwood (IL)
2	urban	Chicago - Jardine (IL)
		Milwaukee - SE Hdqs and UWM-North (WI)
		Gary - IITRI (IN)
3	peak	Harrington Beach (WI)
	concentration	Northbrook (IL)
		Holland (MI)
4	downwind	Zion (IL)
		Manitowoc (WI)
	upper air	Zion (IL)

Supplemental measurements planned for 2002 and beyond include aircraft sampling in the Lake Michigan area by Wisconsin DNR and by Bob Jacko (Purdue University); aircraft sampling in other nearby areas by Bob Jacko (Purdue University); tall building measurements (Sears Tower); operation of an ozone monitor on the Badger ferry (between Manitowoc, Wisconsin and Ludington, Michigan); operation of an open path monitor at Northbrook to provide real time measurements of VOC and carbonyl; and operation of visibility cameras at several sites. Table 2 summarizes the site locations and parameters for the base and supplemental measurements.

## III. REGIONAL AIR TOXICS MONITORING NETWORK

The regional air toxics monitoring network builds upon the individual state air toxics monitoring programs and an initial 5-state monitoring network. The initial 5-state network will include at least one site in Illinois, Indiana, Michigan, Ohio, and Wisconsin and will be consistent with the FY2000 Air Toxic Pilot Program. This monitoring will start in early 2002, and will collect data to assess "community-oriented" population exposures. The goals of the initial 5-state network and the proposed regional network are as follows:

- measure the same 18 "core" compounds identified for the FY2000 Air Toxic Pilot Program;
- sample on a every-sixth day schedule;
- sampling duration of 24 hours (but may be shorter or longer depending on the particular objectives and consideration of detection limits);
- similar monitor siting criteria;
- same analytical methods as in the FY2000 Air Toxic Pilot Program;
- state laboratory inter-comparisons to be conducted using split samples and canister exchanges, and the results applied to historical Region V air toxics data; and

 same quality assurance practices as in the FY2000 Air Toxic Pilot Program to be employed.

Table 3 lists the monitoring site information, pollutants to be measured, sampling schedule, and sampling/analysis methods for the initial 5-state network. It is envisioned that the regional network will expand the initial 5-state network. Note, based on the cost estimates for the initial 5-state network (i.e., about 60K/site), a regional network of say, 5-10 sites per state, will cost about 1.8-3.6M per year. Additional funding will be needed to pay for this monitoring. (Please note that these plans are subject to change based on forthcoming guidance on the national air toxics monitoring network.)

#### IV. RECOMMENDED REGULATION CHANGES

The elimination of several sites above will require a waiver from certain monitoring requirements in 40 CFR Part 58, Appendix D (Network Design for State and Local Air Monitoring Stations [SLAMS], National Air Monitoring Stations [NAMS], and Photochemical Assessment Monitoring Stations [PAMS]):

- Section 3.2 (SO2 Design Criteria for NAMS): waive the requirement for 2 4 monitors in urban areas with population > 1,000,000 and low concentrations, and for 1 2 monitors in urban areas with population 500,000 1,000,000 and low concentrations
- C Section 3.3 (CO Design Criteria for NAMS): waive the requirement for a micro-scale, and/or middle or neighborhood-scale monitor in urban areas with population > 500,000
- C Section 3.4 (O3 Design Criteria for NAMS): waive the requirement for a downwind monitor for all urban areas with population > 200,000
- Section 3.5 (NO2 Design Criteria for NAMS): waive the requirement for two monitors in urban areas with population > 1,000,000
- Section 4.4 (Network Design for PAMS, Minimum Monitoring Network Requirements): waive the requirement for VOC and carbonyl sampling at Type 1, 3, and 4 sites (or accept the proposed changes as part of an "alternative" network design, as provided by section 4.2)

In addition, consideration should be given to revising the minimum quality assurance requirements. For example, 40 CFR Part 58 requires bi-weekly precision checks for automated methods. A reduction in the number of checks is recommended, especially for monitors that measure concentrations below the NAAQS.

#### V. NEW TECHNOLOGY

The states are committed to the evaluation and deployment of new monitoring technology, especially for PM2.5 and air toxics. To this end, the following new technology is being used (or considered) by the states:

IL OPSIS (for formaldehyde, benzene/xylene, and mercury)

Continuous mercury monitor

Modified auto-GC for toxics

Diffusion tubes for toxics saturation monitoring

Glass-lined canisters for VOCs and toxics

MI Hexavalent and total chromium monitors

PAHs using modified PUF sampler

Continuous mercury with TEKRAN (w/ speciation) and LUMINEX

OH Ammonia monitoring

WI Ammonia monitoring

Continuous mercury with TEKRAN analyzer

In addition, most states are establishing visibility cameras (as part of the Midwest "hazecam" network), and continuous PM2.5-mass and continuous PM2.5-speciation monitors.

#### VI. FEEDBACK

This document and the proposed network changes reflect the opinions of the monitoring staff in the Region V States. An important step in the development of the regional monitoring strategy is to get input from the following groups: (1) technical and regulatory staff in the States and USEPA; (2) policy types, especially state air directors; (3) stakeholders, including local government, environmental groups, and private industry; and (4) the general public. Based on this additional input, this document and the proposed network changes will be revisited.

#### VII. SUMMARY OF RECOMMENDATIONS

- A regional air toxics monitoring network should be established.
- States should continue to pursue new technology, especially for PM2.5 and air toxics.
- A number of changes (decreases, increases, relocations, revisions) to the existing state criteria pollutant monitoring networks are proposed.
- A public outreach effort is needed to explain and seek "buy-in" on the proposed changes to the criteria pollutant monitoring networks.
- The resource savings resulting from the proposed changes in a given state will be reinvested in that state. Note also that the resource savings will not be sufficient to pay for the regional air toxics monitoring network. Additional funding will be needed.

- USEPA should revise the NAMS/SLAMS regulations to relieve the states of certain monitoring requirements and to allow some of the proposed network changes.
- USEPA should continue funding for EMPACT to ensure that near real-time information is provided to the public for all air pollutants (especially, PM2.5), as appropriate.

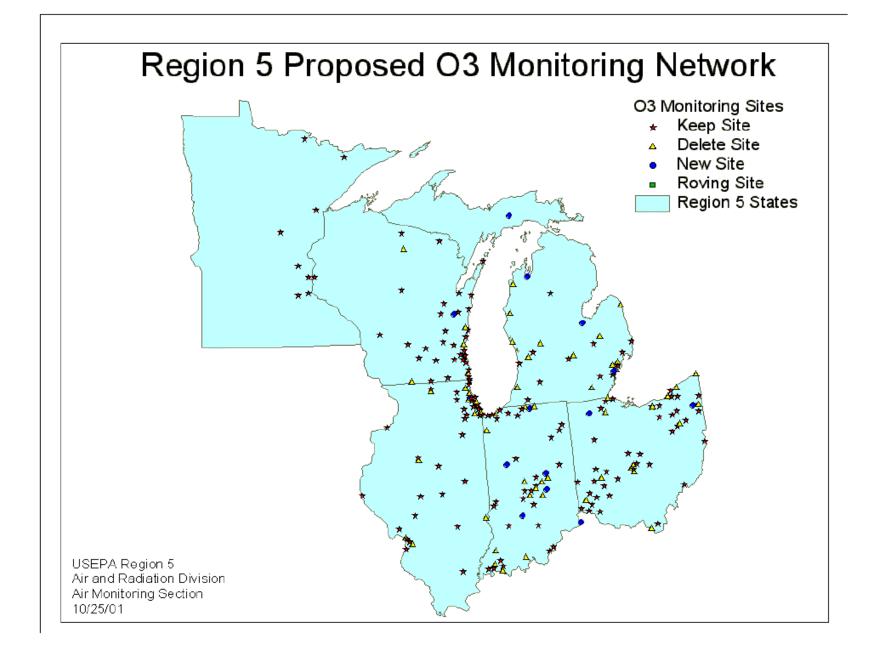
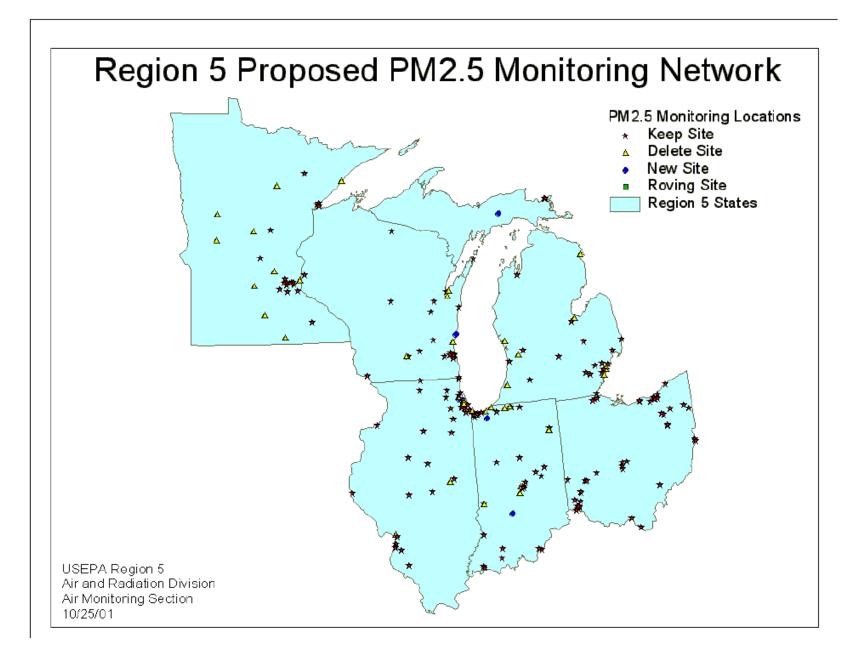
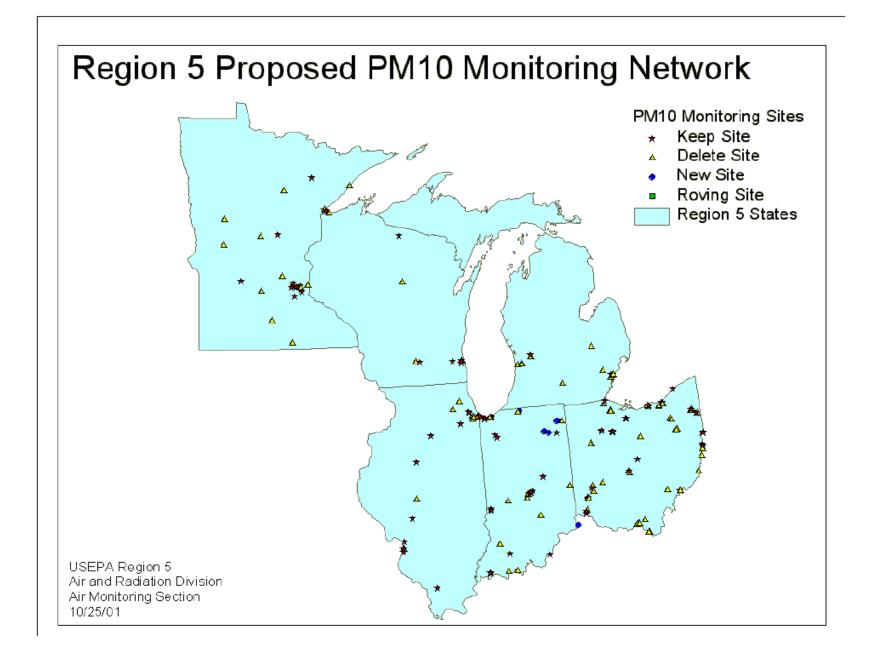
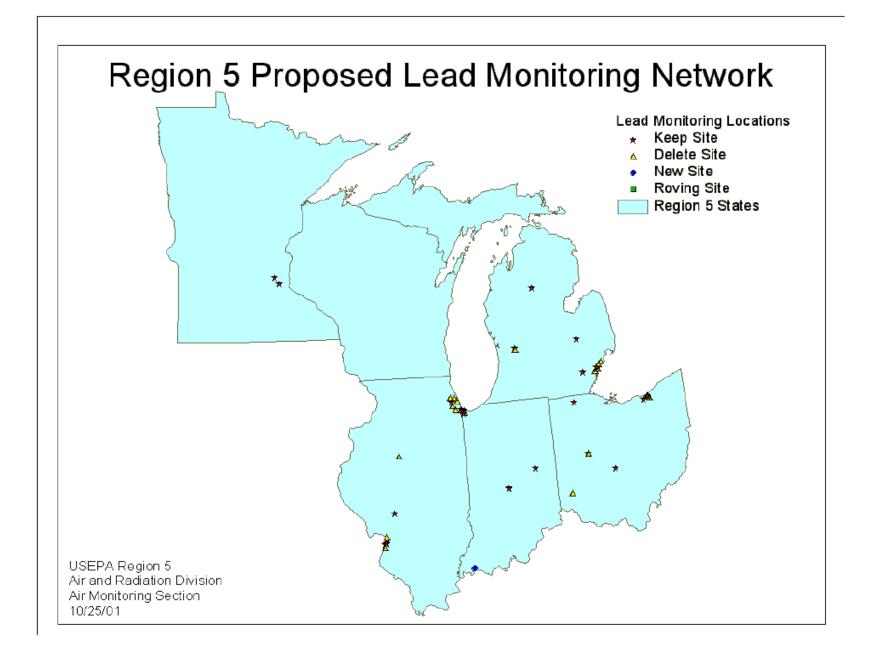


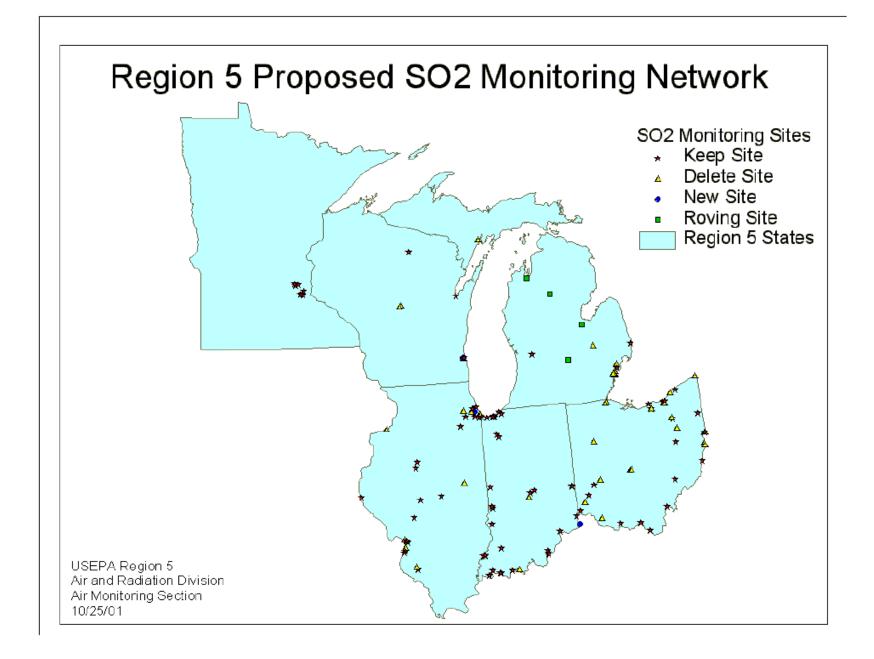
Figure 2

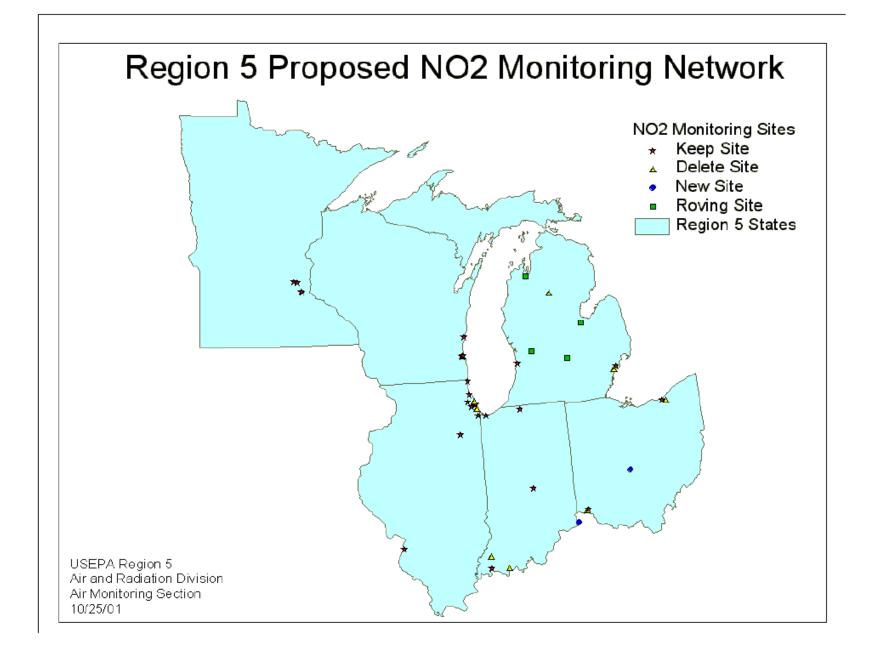


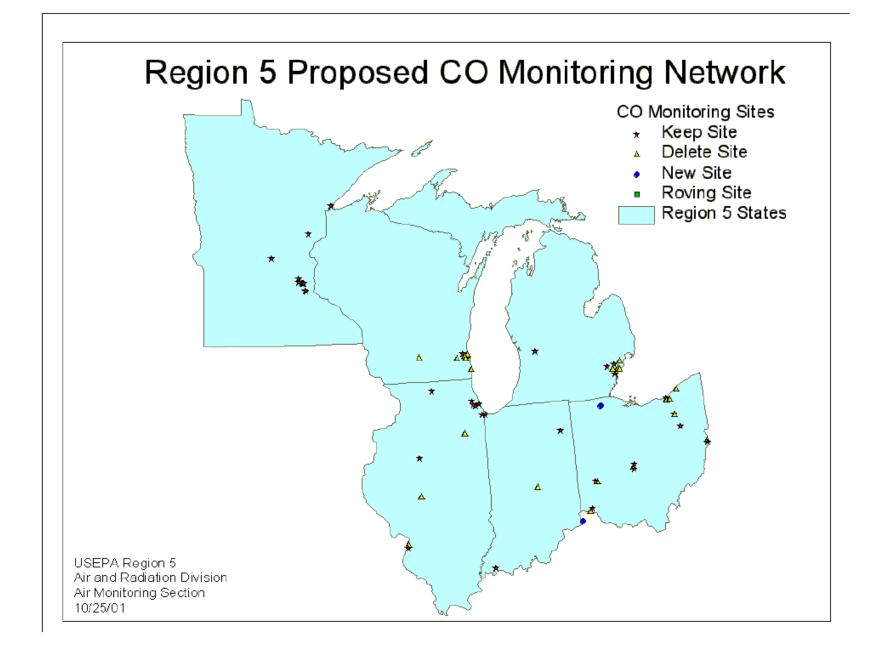




*October 26, 2001* Figure 5







October 26, 2001 Figure 8. Region V Graphical Analyses

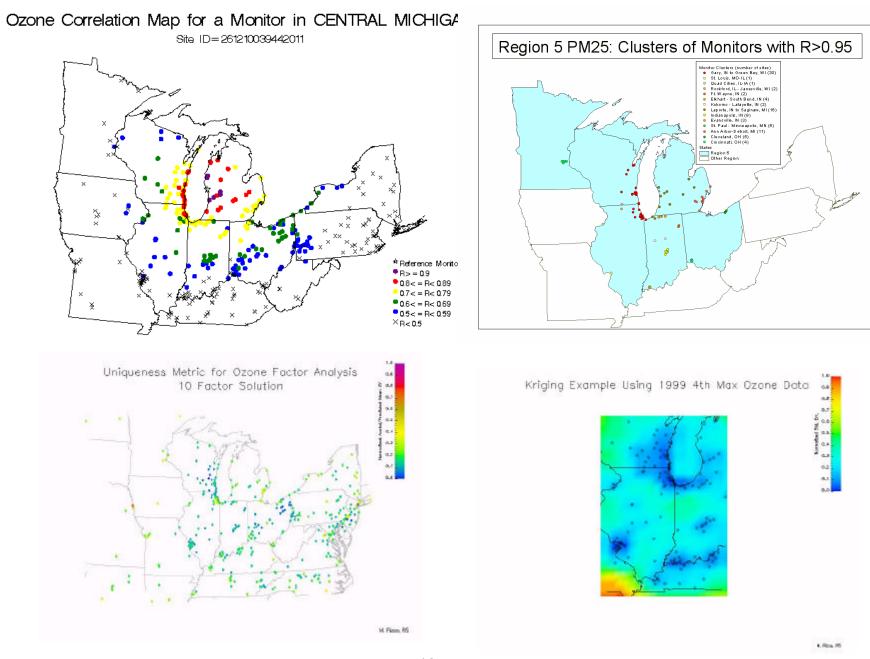


Table 2. Site-Parameter Listing for the Lake Michigan PAMS Network

Site	Туре	О3	NOx	NOy	Met	VOC	Carb.		•	Upper Air Met
Braidwood	1	Χ	Χ	Χ						
Chicago_Jardine	2	X	Χ		Χ	Α	Χ			
Northbrook	3	Χ	Χ		Χ	A,t	X,t	Χ	Χ	
Zion	4	X	X,s	Χ	Χ	Α	Χ			Χ
Milwaukee-SE Hdqs	2	Χ	X,s	Χ		Α	Χ	Χ		
Milwaukee-UWM	2	Χ	Χ		Χ	t	t			
Harrington Beach	3	Χ	Χ		Χ	C (24	-hour s	ample	every (	ີ່5 <sup>h</sup> day)
Manitowoc	4	Χ	X,s	Χ	Χ			Χ		
Gary-IITRI	2	Χ	Χ	Χ	Χ	A,t	X,t	Χ		
Holland	3	Χ	Χ	Χ	Χ			Χ		
WI Aircraft		X		Χ	X,p	С	Χ	Χ		
Jacko Aircraft		Χ			•	С	Χ	Χ		
Sears Tower		X								
Badger Ferry		Χ								

A = auto-GC

C = canister sampling

s = high sensitivity NOx

t = air toxics sampling (24-hour canister sample every 6<sup>th</sup> day year-round)

p = partial met (temp, rel. humidity)

Table 3. Monitoring site information, pollutants to be measured, sampling schedule, and sampling/analysis methods.

	Monitoring Site		Pollutant	Sampling	Sampling		
Urban Area	Street address	AIRS ID	Measured	Schedule	Apparatus/Media	Analytical Method	
Chicago, IL	Water Treatment Plant 750 Dundee Road Northbrook, IL	17-031- 4201	53 VOCs, 14 carbonyls, 8 metals + continuou s Hg	1 in 6 day	VOCs - summa- polished canister, Carbonyls - DNPH cartridge, Metals - TSP (hi-vol) particulate sampler	VOCs - TO-14a gas chromatography, Carbonyls - TO-11a high pressure liguid chromatography, Metals - atomic	
	4743 Mannheim Road Schiller Park, IL	17-031- 3103	53 VOCs, 14 carbonyls, 8 metals	1 in 6 day for carbonyls + metals; VOCs collected on a limited basis (6- 12 sample days selected at random)	using quartz filter	absorption spectroscopy	
Indianapolis, IN	3120 E. 30 <sup>th</sup> St. Washington Park Indianapolis, IN	18-097- 0078	9 "core" VOCs + subset of TO15, 11 carbonyls, 7 metals	1 in 6 day	VOCs - summa- polished canister, Carbonyls - DNPH cartridge, Metals - TSP (hi-vol)	VOCs - TO-15, Carbonyls - TO-11a high pressure liguid chromatography (ERG), Metals - IO-3 - Inductive Coupled Plasma/Mass Spectrometry (RTI)	
Cleveland, OH	Fire Station #22 7300 Superior Ave. Cleveland, OH (St. Clair/Superior neighborhood)	39-035- 0047	71 VOCs, formaldeh yde + acetaldeh yde,	1 in 6 day	VOCs - summa- polished canister, Carbonyls - DNPH cartridge, Metals - TSP (hi-vol)	VOCs - TO-14a gas chromatography, Carbonyls - TO-11a high pressure liguid chromatography	
	Fire Station #11 7629 Broadway Ave. Cleveland, OH (Slavic Village neighborhood)	None	8 metals	1 in 6 day	particulate sampler using glass fiber filter	(contract lab), Metals - acid extracttion followedby inductively coupled plasma emission spectroscopy	
	Board of Education 7733 Stone Rd Independence, OH	None		1 in 12 day			

	Monitoring Site	Pollutant	Sampling	Sampling			
Urban Area	Street address	AIRS ID	Measured	Schedule	Apparatus/Media	Analytical Method	
Detroit, MI	TBD	TBD	18 "core" compound s + other compound s measured during 2000 Detroit pilot	1 in 6 day	VOCs - summa- polished canister, Carbonyls - DNPH cartridge, Metals - TSP (hi-vol) particulate sampler	VOCs - TO-15 gas chromatography, Carbonyls - TO-11a and SW-8315 (MDEQ), Metals - Note: TSP samples to be analyzed as monthly composites.	
Madison, WI	Water Reservoir Dayton & Livingston St. Madison, WI	55-025-0025	34 VOCs 13 carbonyls, total PCBs, 8 metals	1 in 6 day for VOCs + carbonyls; 1 in 12 for metals; 1/12 for PCBs (plus 1/24 from 10/15 to 3/31)	VOCs - pressurized passivated canisters, Carbonyls - DNPH coated silica gel cartridges, PCBs - quartz fiber filters with polyurethane foam back-ups using a General Metal Works PS-1 (hi-vol) sampler, Metals - quartz fiber filters using a General Metal Works TSP sampler	VOCs - TO-14 - cryogenic concentration followed by a single column gas chromatography, Carbonyls - TO-11 - solvent extracted and analyzed by high performance liquid chromatography with UV detection, PCBs - TO-4 - solvent extracted by soxhlet and cleaned extract analyzed by gas chromatography with EC detection, Metals - acid extraction followed by either Inductively Coupled Plasma Emission Spectrophotometry (ICP) or Atomic Absorption Spectrophotometry (AA) Note: Nickel and beryllium to be collected on 72-hour composites samples.	

#### **Section 4. The National Core Network (NCore)**

## 4.1 Background

Air monitoring efforts serve a variety of needs, both national and local. The rationale for even considering national based networks is simply a recognition that a very significant part of any "local" air pollution problem often is associated with some form of long-range transport or part of an extensive region-wide airshed. Similarly, a major component of emissions reduction strategies are based on national programs (e.g., the Federal Motor Vehicle Control Program, Clean Air Act Title IV [acid rain precursors], nitrogen oxide [NOx], SIP calls in the eastern United States, and the recent Clear Skies program. The nature of "national" ambient air quality standards implies an understanding of the cause-effect phenomena between pollutants and adverse health impacts is based on a range of diverse populations and locations throughout the Nation. Numerous national level modeling tools drive a range of air quality prediction and health assessments requiring consistency in measurement approaches.

It is assumed that the need for monitoring to characterize and assess localized air quality issues is comparable to that required for national needs. Therefore, the development of a national network component must allow for needed flexibility to address local issues as well as accommodating emerging technologies and science/policy needs that often are constricted by massive infrastructures. In application, enough overlap exists between national and local design features, such that a network designed for a national purpose more often than not also services a local need. For example, a national speciation trends site is used in concert with other mass and speciation sites for a more detailed local characterization of an area's particulate matter.

#### **4.1.1.** Needed Network Design Enhancements

The Strategy presents an opportunity to reconfigure ambient air monitoring networks to accommodate identified measurement needs and improved technologies. Experience over the last 20 years suggests four basic enhancements that can be implemented in national network design by:

- allowing for multiple and collocated pollutant measurements to better diagnose cause-effect phenomena between public health effects and air pollution and atmospheric processes;
- 2) characterizing regional scale air quality to understand the linkage between background and transport concentrations (regional, continental, global scales) as they affect rural and urban environments. This need has become increasingly important as the separation in pollutant concentrations between rural and urban air pollution levels continue to decrease;

- 3) **accommodating new technologies** to provide timely reporting of air quality information to the public and to improve basic characterization of physical, chemical, temporal, and spatial composition of air quality; and
- 4) **improving flexibility** to: (1) incorporate future monitoring of new pollutants, and (2) meet local air monitoring needs.

Consistent with these enhancements, the NMSC has identified the following areas for enhancement:

- greater characterization of hazardous air pollutants (HAPs);
- additional continuous particulate matter monitoring;
- additional information transfer and delivery to the public; and
- integration across pollutant programs.

This proposal for a National Core (NCore) network is intended as a modest set of actions to accommodate these enhancements, while striving to work within the near-zero-sum framework of the strategy.

## 4.1.2 Rationale for Multi-pollutant Sampling and Spatial Mapping

There are many advantages in shifting toward a multi-pollutant monitoring network. The three main reasons are cited below.

- 1. **Minimizing monitoring site operational expenses**. A central site with several instruments requires far less travel time and site attention and maintenance than a diffuse network, assuming, of course, attendant reductions in single pollutant sites.
- 2. **Fostering integrated air quality management**. For years we have recognized the administrative burden of working in a single pollutant framework, when we understand an array of technical linkages across air pollutant categories. From an emission source perspective, mobile and stationary combustion sources simultaneously emit ozone and PM precursors as well as a host of hazardous air pollutants. Numerous chemical and physical atmospheric processes either link several pollutant categories or operate in parallel. Examples include the shared mix of precursors (i.e., primary emissions), intermediate and sink species that link ozone and fine particulate matter (and haze); the adsorption dynamics where particles act as carriers of various hazardous air pollutants; numerous transformations where oxidant precursors (e.g., xylene, toluene, pinenes) are capable of transforming into organic aerosols, specific HAP compounds such as formaldehyde that act as an ozone precursor and through chemical pathways influence particle formation. The list of examples is endless and provides a motivation for integration. However, the intention is not to imply that every aspect of air pollution is integrated as such linkages often exhibit a variety of seasonal and

location dependencies. Nevertheless, the historical emphasis on single pollutant programs needs to move toward more integrated approaches, and air monitoring is a key air program infrastructure component that should facilitate progress.

3. Supporting national level air quality models and health assessments. Two examples are provided:

#### **Example 1. Air Quality Model Simulation evaluation:**

Air quality simulation models (AQSMs) combine an array of emissions, atmospheric chemical and physical dynamics to serve as important tools for developing emission control strategies and attainment demonstrations. The structure of AQSMs is based on an integrated multi-pollutant framework. Questions have been raised regarding the role of routine networks in evaluating models. For example, diagnostic (e.g., stressing the model to determine if it reproduces observations for the right reasons) model evaluation requires short period intensive field campaigns incorporating vertical chemical/physical profiling throughout the troposphere and research grade measurements of complex radical and sink species, typically beyond the scope of SLT operated routine networks. Diagnostic model evaluation complements the need for basic operational (i.e., does the model generally reproduce observations of important precursor and product species) AQSM evaluations that may span an entire year or more, and be subject to specific episodes of concern not covered in an intensive field campaign. Nevertheless, there have been misconceptions associated with the relevancy of routine data in the model evaluation process and concerns that routine operations be moved toward more "research" grade measurements to support modeling. Some of this concern is perhaps traced back to the role of ozone models in estimating the high 1-hour prediction. Comfort levels on model performance were focused on a few summer-based high concentration episodes, and model performance during other seasons was not a priority. The change in ozone standards to a lower value 8-hour average, and the dominance of the annual PM2.5 standard require our models to perform well (and be evaluated) over more diverse time and meteorological regimes. Moreover, the large regional behavior of ozone and PM<sub>2.5</sub> present national level issues that result in the AOSMs (e.g., CMAModels 3, REMSAD) applied over large spatial domains covering the entire contiguous United States. As the models are now applied over increasingly larger spatial and time scales, the monitoring networks must adopt and provide a minimum level of support for their evaluation. Finally, an infrastructure of routine measurements, even during those intensive field campaigns designed for diagnostic model evaluation, are required.

Three very critical components of NCore address the model evaluation needs: spatial mapping, multi-pollutant measurements and continuous data. From an operational model evaluation perspective, models attempt to replicate major

surface scale features of the primary pollutants of interest, largely PM2.5 and ozone. The emphasis on mapping as a national need for public information purposes is just as critical for AQSM evaluation, as well as other emissions strategy elements (e.g., defining planning areas and tracking progress over time) and health and exposure assessments. (See example 2.) The leveraging of collocated pollutants improves the ability to evaluate models by providing greater challenge to testing more than one State variable at a time. In effect, the availability of important collocated species restricts the ability to subjectively improve model performance and can serve to identify areas need for improvement. The core multi-pollutant species were chosen as key species from both model evaluation and health assessment perspectives. Finally, the emphasis on continuous data is valued from a model evaluation perspective. Although one role of a model may be to estimate an annual average, AQSMs generally calculate predictions over small time intervals and typically can provide output at one-hour time intervals. The ability to test model's temporal behavior benefits both short and long-term predictive ability as errors at small time scales can aggregate easily to cause problems over large time scales.

While this discussion has emphasized the use of data in evaluating model performance, a far more important integration across observations and models must be fostered through the air quality community. Calculated model concentrations and observations are all predictions: they just use different tools or formulations to arrive at the same product. A point measurement based on "measurement determined" observation is perhaps no more representative of the larger area of volume of concern than that developed through a "model." In a sense, modeled data and measured data all are predictive results from the spatial and temporal perspective from which we interpret data. We need to make much better progress in integrating modeling and monitoring techniques and take advantage of the maximum benefits derived from their highly synergistic usage. An opportunity is now presented to meld real-time modeling data that are corrected or "nudged" by the observations to produce our best and most timely representations of more complete spatial surfaces. Such surfaces are part of the future vision for linking observations and model predictions through the information transfer initiative being conducted nationally through NCore. Similarly, the use of spatial fields have multiple benefits for air quality planning and tracking which will improve with our ability to characterize spatial fields over frequent time intervals.

Other observational techniques benefits from NCore multi-pollutant sites, and include source apportionment models that connect emission source categories with receptors (measurements) and observational based models (OBMs) that use measurements to infer precursor control preferences (e.g., NOx or VOC for ozone; NH3 or NOx for PM). Again, these tools as well as predictive models all together require basic inputs and checks for their operation.

Collectively, with direct observations all the modeling tools applied in both traditional and unique means are used in "weight-of- evidence" schemes to develop practical emission reductions strategies.

### Example 2. Health and exposure assessments for NAAQS reviews

Many of the arguments for model evaluation apply to exposure and health assessments. First, we have a national need to maintain a minimum core network to support long-term exposure and epidemiological assessments that factor into the recurring 5-year reviews of the NAAQS. To be clear, NCore supplies only a basic infrastructure of routine measurements, not personal or indoor monitoring that is necessary for exposure assessments. NCore will, however, provide key centralized monitoring data from which to relate back to more detailed microscale and other ambient exposure related measurements. Similarly, NCore will not collect all of the suspected particulate-matter-related agents hypothesized to be key players in the direct adverse health impacts associated with PM (e.g., soluble metals, ultra fine particles, and biological matter). Health assessments attempt to develop causative relationships between specific air pollution parameters and adverse health effects, which benefits from sampling a variety of pollutants over a range of diverse populations, covering different air quality conditions brought on by different climatologies and emissions patterns (i.e., mix and strengths of source types). Multiple pollutant species need to be sampled at different locations to better delineate the effects of a particular species by teasing out a range of confounding factors associated with interactive effects among different pollutants. Accordingly, NCore should measure multiple pollutants across a diverse group of platforms reflecting a range of populations, climatology and air quality composition across the United States.

## 4.2 Attributes of NCore

The NCore network is envisioned to be a long-standing stable network that should be viewed as a "minimum" infrastructure to address major national monitoring objectives. These national objectives and other attributes are used as a starting point for design. In describing national objectives, a substantial degree of overlap with areaspecific objectives in aspects of network design will emerge. That is part of the overall optimization and leveraging that is intended. The scope of this activity retains the focus on traditional networks operated by SLTs. National needs beyond these that include ecosystem welfare assessments, global atmospheric transport and diagnostic research need to be integrated as part of the leveraging optimization process (addressed later in this section).

In developing the overall objectives for the Strategy, the NMSC also developed objectives for the NCore component, and these objectives are referred to as "attributes," so as not to be confused with the Strategy objectives. The NCore attributes are as follows:

- To satisfy the minimal level of national ambient air monitoring needs, including:
  - real-time input of data from across the country (e.g., AIRNow) using continuous technologies for timely dissemination to the public and supporting:
    - spatial mapping
    - public health advisories
    - public air quality forecasts
  - o emissions strategy development, including:
    - routine/operational model evaluation
    - observational and source apportionment techniques
    - defining nonattainment and emissions strategy regions
  - o tracking air quality trends and progress, such as
    - accountability of major national emissions strategies
    - health/welfare assessments (e.g., for HAPS, visibility)
  - o NAAQS determinations (i.e., compliance with standards)
  - health assessments that influence periodic NAAQS reviews (i.e., 5-yr EPA review process)
- To provide a consistent national network of multi-pollutant measuring sites;
- To provide consistent air quality information for both urban and rural areas;
- To provide a basis from which the augmentation by state/local/tribal monitoring networks can be utilized to meet SLT monitoring priorities;
- To accommodate the national needs for monitoring new pollutants (e.g., air toxics, PM<sub>(10-2.5)</sub>);
- To maximize leveraging of existing air monitoring sites, especially those with multi-pollutant capabilities; and
- To the degree it can be accommodated, provide data and other support for essential science needs, such as:
  - o health/exposure studies
  - o evaluation of new monitoring methods
  - characterization of atmospheric processes and source-receptor relationships (e.g., air quality model evaluation; source characterization techniques).

#### 4.3 The National Component

NCore is intended to address national level data needs that often are a secondary concern of historical networks that were designed from a single pollutant and often local

area perspective. NCore does not address explicitly those monitoring needs associated with a local/flexible component. Rather, by defining a modest national network, the capacity (or flexibility) to support local needs is protected. Additional discussion on this balance between national and local needs is provided below and in the document summary. Throughout this document there is far more discussion addressing "national" needs, a natural outcome as all parties have a vested interest in a larger national picture. However, this emphasis on national needs should not be construed as elevating national over local needs. Details of the attributes for the national component are given below.

#### **4.3.1** Public Information

The acquisition of real-time data from across the country (e.g., through AIRNow) using continuous technologies for timely dissemination to the public is a central element to NCore. Such information could drive national mapping programs for PM2.5 and ozone reported from AIRNow, and further support public air quality forecasts and public health advisories for various pollutants. To date, AIRNow has effectively used and evolved into a national resource built upon available data sources from an array of State and local networks designed for non-mapping purposes. By specifying mapping as a national objective, network spatial design tools can be applied to optimize the existing networks with a cohesive central mapping theme that lends itself to other applications, including emission strategy development and compliance.

## **4.3.2** Emissions Strategy Development

The development of emission reduction strategies relies on large regional to national scale air quality simulation models as one of several tools in combination with various area-specific analyses. Models require evaluations which occur at different spatial scales and levels of complexity. National level models often undergo fairly routine "operational" level evaluations that rely on routinely collected data. These routine operational evaluations complement more complex diagnostic evaluations utilizing aircraft data, and research grade measurements of atmospheric intermediate and end products. In application, three types of monitoring approaches are used for model evaluation. First, the NCore component would support much of the operational evaluations of Air Quality Simulation Models (AQSMs), principally by ensuring broad and consistent geographic coverage. Second, the availability of routine data from local oriented networks and mapping related networks (e.g., AIRNow) would enhance the spatial richness of observations for evaluation purposes. And third, routine measurements from NCore would complement intensive field campaigns that provide more complex detailed measurements (e.g., time, space and composition) for diagnostic evaluations.

Numerous source apportionment and other observation-driven models attempt to use measurements directly to associate source-receptor effects and infer emissions reduction approaches even in nonlinear systems. While the application of these tools tend to be area specific, the availability of NCore sites that include multiple collocated

measurements will provide significant benefits and also allow for consistent national level applications.

Mapping tools delivering public information should strive to minimize concentration surface error and produce coherent pollutant concentration patterns which can guide emissions strategy development.

## 4.3.3. Tracking Air Quality Trends and Emissions Strategy Progress

NCore would provide the primary input to track national air quality trends of a range of noncriteria and precursor pollutants as reported in EPA's annual air quality trends and related reports. NCore also would accommodate an important accountability component of air quality trends, which tend to place somewhat greater emphasis on directly emitted precursor species to determine if emission strategies are being implemented as originally intended. For accountability purposes, consideration must be given to locating some NCore sites in rural representative locations with instrumentation capable of detecting long term emission changes associated with implementation of national programs such as Title IV, the NOx SIP calls, and the Clear Skies program (nitrogen, sulfur, mercury). Program tracking also would include national visibility assessments as well as a selected limited group of hazardous air pollutants (HAPs) that tend to be of concern in numerous locations nationwide.

## 4.3.4. Support Health Assessments and Periodic NAAQS Reviews

Historically, much of the underlying health effects research has relied on routinely available data to associate various adverse health impacts with air quality. NCore would provide a diversity of monitoring locations across the nation to provide a stable base of data for long-term health assessments. (See, for example, Attachment 4-1, "Air Quality Monitoring in Support of Epidemiology.") These health assessments require basic "representative" air quality data of several common pollutants across a diversity of population and emission regimes. The NCore design will emphasize the importance of capturing diverse locations and provide a minimum group of routinely collocated measurements that will assist both health assessment and emissions strategy development needs. More advanced air quality measurements would be conducted through collaborative research endeavors and not directly supported by state/local agencies and Tribes. However, where possible the development of NCore platforms should anticipate the need for possible collaborative work ranging from toxicologists choosing to collect occasional "mega" aerosol samples, to atmospheric scientists conducting research grade measurement studies. Therefore, platform capacity, space and power specifications, generally should be designed to avoid future extensive retrofitting.

#### 4.3.5 Compliance

NCore will be used for basic comparisons to the NAAQS. Traditionally, monitoring for NAAQS comparisons has been more of a localized objective brought about by national regulations. Increasingly, the extent of non-attainment for our

principal criteria pollutants (i.e., PM<sub>2.5</sub> and ozone) has become, in many instances, more of a regionalized issue due to numerous factors including shifting demographics away from urban centers, widespread homogeneous behaviors of PM<sub>2.5</sub> aerosols in many eastern U.S. locations, and the shift to a lower concentration 8-hour ozone NAAQS. Here again, the characterization of concentration surfaces through mapping requires both national and local perspectives.

## 4.3.6 Support Science Studies

Many of the previous objectives discussed the complementary role routine networks play in supporting research. Routine data generally complement more intensive research-oriented efforts spanning a range of atmospheric process and health assessment studies. While NCore design will be driven to address non-research objectives, the overlap between research and regulatory needs is substantive and it is imperative that NCore be viewed as an important research resource. To that end, components of the NCore network should facilitate collaborative work with research institutions in a manner similar to the Supersite program for PM<sub>2.5</sub>. Certain NCore platforms could serve an important instrument evaluation need at a national level. NCore will therefore include a limited number (probably in the order of 3 to 8) of collocated multi-pollutant sites that serve primarily the scientific objectives listed above. Collocation also provides opportunities for diagnosing measurement methodology issues as the more complete characterization of atmospheric chemistry provides enormous insight into likely causes of measurement artifacts. The concept is not that routine grant programs for state/local/ agencies and Tribes siphon their resources to support research institutions, but rather that a greater level of complementary work across research and regulatory agencies is engendered as part of the NCore design which provides more optimized benefits for all parties. As platform capacity is reviewed for accommodating new measurements, enhanced capacity should be built in for collaborative work where researchers may need to use platforms for short periods of time to collect large samples of aerosols for toxicological studies, or operate research grade measurements in concert with more routine instrumentation.

Other broad based national air monitoring objectives include ecosystem welfare assessments, characterization of global/continental level transport phenomena, and explicit research objectives. The objectives listed above are compatible with the existing federal grant structure, where Section 103 and 105 Grants are administered by EPA to state and local agencies, and Tribes. Nevertheless, significant integration and optimization opportunities exist to link with these other major national objectives.

## **4.4** The Local Component

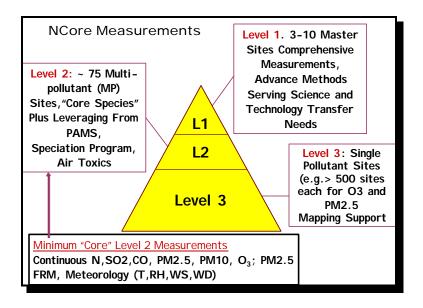
The development of NCore does not replace the role of localized networks, and no premise is made on the relative importance of national versus local needs. In looking at the local component, the NMSC established several objectives, or attributes, to clearly delineate the intent to address local concerns. The following listing of attributes

illustrates some of the major differences between the national NCore component and the more flexible component of state/local/tribal networks:

- To address state/local/tribal concerns not adequately addressed through NCore. Examples include:
  - o "hot spot" or mobile monitoring for air toxics
  - o source-specific monitoring
  - o community/environmental justice concerns
  - o emissions reduction strategy assessments
  - o tracking non-criteria pollutants of concern
  - o NAAQS designation requests
  - o enhanced monitoring as needed for local characterizations of key pollutants and/or their precursors
- To establish the highest priorities for state/local/tribal air monitoring needs and
  utilize local flexibility to shift resources to meet those needs, including the
  reduction of inefficient monitors and the addition of value-added monitors as
  necessary.
- To utilize data such that the benefits of the NCore network can be enhanced.
- To meet federally-recommended monitoring objectives to the degree possible.

#### 4.5 NCore Structure

NCore would be structured as a three-tiered approach (see Figure 4-1), based on measurement complexity, ranging from the most (Level 1) to the least (Level 3) complex. A range of 3 to 10 Level 1 "master" sites, based on available resources, would serve a strong science and technology transfer role for the network. Approximately 75 Level 2 sites would add a new multiple pollutant component to the networks, with emphasis on continuously operating instruments. In many areas, location of a Level 2 site, as appropriate, in conjunction with existing PM speciation, PAMS and/or air toxics trends sites, would optimize leveraging of existing resources to meet Level 2 objectives. Level 3 sites are largely single pollutant sites, emphasizing the need for a spatially rich network in the most ubiquitous criteria pollutants (i.e., PM<sub>2.5</sub> and ozone) and addressing an assortment of compliance related needs. Progressing from Levels 1 through 3, the character of these sites moves from a strong science orientation toward compliance. A summary of measurement parameters for these levels is provided in Table 4-1.



**FIGURE 4.1** Components of NCore.

#### 4.5.1. Level 1

There would be a small number (e.g., 3 to 10) of Level 1 "master" sites, or "supersites," which would include the most comprehensive list of routine measurements required for the Level 2 sites (see next subsection), plus research level measurements with potential for routine application (e.g., PM size distribution, nitric acid, ammonia, true NO<sub>2</sub>). Level 1 sites could include additional measurements dependent on areaspecific priorities, available expertise, and resources. These sites would serve three needs: (1) a comprehensive suite of measurements providing the most insightful of all routine air monitoring networks; (2) a technology transfer mechanism to test emerging methods at a few locations with disparate conditions that eventually would find more mainstream application<sup>2</sup> and (3) a bridge across routine applications and science.

Over the last 10 years, EPA's Office of Research and Development has gradually decreased its level of methods development and testing to a point where it no longer is considered a leader in this field. Methods testing now is conducted through a rather loose collection of state-sponsored trials (especially California's Air Resources Board), vendor sponsored initiatives, miscellaneous research grants, and agreements to

<sup>&</sup>lt;sup>1</sup>NO and NOy are chosen as they provide indicators for relatively fresh (NO) and aged (NOy) emissions. They provide a critical tool in accounting for progress in large-scale nitrogen emission reduction programs (e.g., NOx SIP calls and Clear Skies, provide input for a variety of observational based and source apportionment models, and assist evaluation of air quality models. True nitrogen dioxide, NO<sub>2</sub>, should be added as a core measurement. However, the lack of affordable and routinely operational instrumentation prevents such a recommendation at this time.

<sup>&</sup>lt;sup>2</sup>True nitrogen dioxide measurements should be part of routine operations; however, field testing and demonstration efforts must precede application in routine networks. Consideration for future routine applications should also be given to other measurements such as continuous ammonia, nitric acid, and particle size distributions.

universities (e.g., PM Supersites and health centers), combined with a skeleton level of effort of internal EPA testing. The PM Supersites program does fulfill some of the needed technology transfer needs, but is of short duration and mostly focused on a broad array of particle characterization issues in addition to technology testing. Level 1 sites would be one component addressing this national level weakness that needs attention. State agencies cannot continue to be burdened with being "trial" testers of new methods. More importantly, there is a pressing need to avoid losing the opportunities in greatly enhanced data value that emerging technologies present.

#### 4.5.2. Level 2

Level 2 measurements represent the mainstream multiple pollutant, or "backbone," sites in the network. The approximate total number of 75 national sites, as well as the proposed measurements, is a modest recommendation. This approach introduces a reasonable and manageable realignment in the networks. Site locations will be based on design criteria that balance technical needs with practical considerations such as leveraging established sites and maintaining geographic equity. There are key design features which embody the purpose of the Level 2 sites:

#### 1. Use of continuously operating instruments:

Continuous systems allow for immediate data delivery through state-of-the-art telemetry transfer and support reporting mechanisms such as AIRNow and a variety of public health and monitoring agencies charged with informing the public on air quality. Continuous data add considerable insight to health assessments that address a variety of averaging times, source apportionment studies that relate impacts to direct emission sources, and air quality models that need to perform adequately over a variety of time scales to increase confidence in projected emissions control scenarios.

#### 2. Diversity of "representative" locations:

Diversity across urban (e.g., large and medium size cities) and rural locations is essential to properly characterize typical urban environments as well as background and transport corridors. National level health assessments and air quality model evaluations require data representative of broad urban (e.g., 5 to 40 km) and regional/rural (> 50 km) spatial scales. Long-term epidemiological studies that support the review of national ambient air quality standards benefit from a variety of airshed characteristics across different population regimes. The NCore Level 2 sites should be perceived as developing a representative report card on air quality across the nation, capable of delineating differences among geographic and climatological regions. While "high" concentration levels will characterize many urban areas in NCore, it is important to include cities that also experience less elevated pollution levels, or differing mixtures of pollutants for more statistically robust assessments. It also is important to characterize rural/regional environments to understand background conditions, transport corridors, regional-urban dynamics, and influences of global transport. Air quality modeling domains continue to increase. Throughout the 1970's and

1980's, localized source-oriented dispersion modeling evolved into broader urban scale modeling (e.g., EKMA and urban airshed modeling for ozone), to regional approaches in the 1980's and 1990's (e.g., Regional Oxidant [ROM] and Acid Deposition [RADM] Models), to current national scale approaches (Models 3-CMAQ), and eventually to routine applications of continental/global scale models. The movement toward broader spatial scale models coincides with increased importance of the regional/rural/transport environment on urban conditions. As peak urban air pollution levels decline, slowly increasing background levels impart greater relative influence on air quality. Models need to capture these rural attributes to be successful to provide accurate urban concentrations.

#### 3. Collocated multiple pollutant measurements:

Air pollution phenomena involving ozone, particulate matter, other criteria pollutants, and air toxics are more integrated than the existing single pollutant program infrastructure suggests. From an emissions source perspective, multiple pollutants or their precursors are released simultaneously (e.g., combustion plume with nitrogen, carbon, hydrocarbon, mercury and sulfur gases and particulate matter). Meteorological processes that shape pollutant movement, atmospheric transformations, and removal act on all pollutants. Numerous chemical/physical interactions exist underlying the dynamics of particle and ozone formation and the adherence of air toxics on surfaces of particles. The overwhelming programmatic and scientific interactions across pollutants demand a movement toward integrated air quality management. Collocated air monitoring will benefit health assessments, emission strategy development and monitoring. Health studies with access to multiple pollutant data will be better positioned to tease out confounding effects of different pollutants, particularly when a variety concentration, composition, and population types are included. The tools for strategy development (e.g., air quality models and source attribution methods) are enhanced by utilizing more robust evaluations (i.e., checking performance on several variables to ensure model produces results for correct reasons and not through compensating errors). Just as emission sources are characterized by a multiplicity of pollutant release, related source apportionment models yield more conclusive results from use of multiple measurements. Monitoring operations benefit by a streamlining of operations and by multiple measurements which can potentially diagnose factors affecting instrument behavior. In addition, the movement toward integrating continuous PM (mass and speciation) monitors, at this juncture, requires care in preserving at least some number of collocated filter and continuous instruments.

The minimum recommended measurements, through near-continuous monitors reporting at 1-hour intervals or less, include gaseous sulfur dioxide ( $SO_2$ ), carbon monoxide (CO), nitrogen oxide and total reactive nitrogen (NO and NOx or NOy), ozone ( $O_3$ );  $PM_{2.5}$ ; and  $PM_{10}$ . Additional parameters include filter-based  $PM_{2.5}$ , as measured with FRMs, and basic meteorological parameters (temperature, relative humidity, wind speed and direction). While these parameters include most criteria pollutants, except for

nitrogen dioxide and lead, they are not chosen for compliance purposes. They represent a robust set of indicators that support multiple objectives of NCore. In most cases, these minimum measurements will be accompanied with measurements from other existing programs, such as PAMS or PM speciation to maximize the leveraging of greater multipollutant availability.

The continuous PM measurements are not expected to use FRM monitors, as currently, no  $PM_{2.5}$  continuous monitor has equivalency status. The reason for specifying continuous methods for PM has been addressed at length. The intention here is not to produce independent  $PM_{10}$  values, but to provide a mechanism to develop an organized and consistent  $PM_{(10-2.5)}$  data base that will be supportive of health studies and emission strategy development. As a peripheral benefit, the development of this data base should meet equivalency testing requirements for a  $PM_{(10-2.5)}$  method and perhaps be viewed as the default "regulatory" method for  $PM_{(10-2.5)}$ . Collocation with FRMs is an important component of the  $PM_{2.5}$  continuous implementation strategy, as the relationship between FRMs and continuous monitors drives the integration of these systems. These relationships will vary in place and time as a function of aerosol composition (e.g., gradual evolution of a more volatile aerosol in the East as carbon and nitrate fractions increase relative to more stable sulfate fraction).

#### 4.5.2.1. Future NCore Level 2 Measurements

The minimum recommended NCore Level 2 measurements reflect a balance across a constrained resource pool, available monitoring technologies, and desired measurements. Consideration should be given to introducing additional Level 2 measurements at selected sites in the future. Examples of nationally important measurements that support multiple objectives include true nitrogen dioxide, nitric acid and ammonia gases. Consideration also should be given to routine size distribution measurements at selected locations. As multiple pollutant stations, NCore sites should over-design for space and power consumption with the expectation of additional future measurements. Such over-design will encourage collaboration between research scientists and government agencies as NCore Level 2 sites should accommodate periodic visits from health and atmospheric scientists that may conduct specialized intensive sampling.

#### 4.5.3. Level 3

Level 3 sites are intended to meet the needs for greater monitoring density for the key pollutants of concern, which currently is ozone, PM<sub>2.5</sub>, and in some areas, mainly in the west, PM<sub>10</sub>. Also, some highly localized carbon monoxide nonattainment areas may still exist. For these key pollutants, and for those nonattainment areas, it is still necessary to maintain a sufficient number of monitors to address the issues associated with SIP development and compliance, as well as other related issues. The Level 3 monitors, therefore, primarily fit this purpose. Such monitors can be single or multi-pollutant, as needed, to address the issues of concern. Examples of conditions, which the Level 3 monitors can address, include:

- documenting the site with the highest concentration
- determining appropriate nonattainment boundaries
- determining local background conditions
- estimating population exposure
- characterizing local conditions
- determining trends
- complementing Level-2 sites in assessing effectiveness of local emissions reduction programs

It is expected that the Level 3 sites will be comprised primarily of existing NAMS/SLAMS sites, since many of the NAMS/SLAMS sites are already satisfying the above set of conditions. The number of Level 3 sites will be based on a combination of local needs and the network assessment process, but clearly, the number of such sites nationally will be far greater than the number of Level 1 and 2 sites.

It is further expected that, at a minimum, new information transfer technologies can be incorporated into the Level 3 sites so that the rapid transfer of data to the public is accomplished consistent with the objectives of the Strategy. To that end, even though the total number of monitors will be less than now exists, the number of monitors reporting, for example, to AIRNow or local websites, should increase over what is readily available today.

Tab	Table 4- 1: Detailed list of NCore measurements					
Site level {Approximate site total*}			Parameter	comments		
L	Level 2 "core" Level 3 (one of) {500 -800}		ozone			
E V E L		PM2.5	Continuous and filter at level 2 sites; emphasis on continuous at Level 3 sites for AIRNow			
1			Basic <u>Meteorology</u>	temp, RH, ws,wd, [surface level]		
3 to 10			<u>PM10</u>	continuous; only filter based at critical Level 2 sites with potential NAAQS (future) violations		
			<u>co</u>	requires funding		
			<u>SO2</u>	requires funding		
			NO/NOy	requires funding		
	Level 2 core plus standard speciation {40-70}		Filter based PM2.5 speciation as in trends	every third day, 24 hr sample; major ions through IC; elements through XRF, EC and OC fractions through combustion		
core plus standard and continuous speciation {10}			daily/continuo us PM2.5 speciation	includes the 10-15 continuous nitrate, sulfate and carbon measurement sites that were added to speciation trends as part of earlier agreements with NAS/CASAC		
	core plus "national HAPs and standard speciation {10-25}	# sites dependent on number of HAPs trends and degree of collocation across speciation	formaldehyde	currently <b>proposed national</b>		
			benzene	HAPs trends measurements to be collocated with PM2.5		
			acrolein	speciation (some unknown subset of daily speciation sites		
			chromium	included)		
			light absorbing aerosol			

core plus speciation and PAMS {15-25}		VOC	minimum PAMS also includes Level 2 core species CO and NO/NOx/NOy; recommend both continuous TNMOC (year round to support HAPs surrogate) analyzer and mix of annual/seasonal canister or auto GC sampling for specific compoundsone type 2 site per current PAMS city
core plus speciation plus PAMS plus HAPS {8-20}	Number of sites dependent on ability to collocate	all of above	
Level 1 specific	Level 1 sites include all above measurements plus next column	real NO2	not routine measurements at this time
		nitric acid	
		ammonia	
		PM size distribution	
		PM ultra fine	
		SVOC	

part of level 3
\_\_\_instrumentation resources required...see section 4.12

#### 4.6 NCore Siting

#### 4.6.1 Level 2

The siting goal for Level 2 NCore sites is to produce a sample of representative measurement stations to service multiple objectives. Siting objectives include:

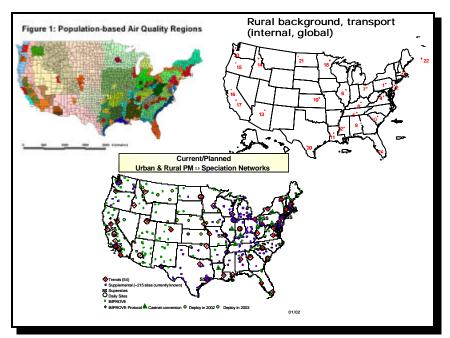
#### A. Collectively:

- approximately 75 locations predominantly urban with 10-20 rural/regional sites:
- for urban areas, across-section of urban cities, emphasizing major areas with > 1,000,000 population, and including a mix of large (500,000 1 million) and medium (250,000 500,000) with geographically and air quality diverse locations suitable as reference sites for long-term purposes;
- for rural areas, capturing important transport corridors, both internal, acrossborder (e.g., Canada and Mexico), and intercontinental, as well as background regionally representative conditions. In addition, some sites should allow for characterizing urban-regional coupling (e.g., how much additional aerosol does the urban environment add to a larger regional mix).
- On an individual site basis:
  - establishing "representative" locations on a scale of 5 to 15 km for urban sites, and greater than 50 km for rural sites, and not impacted by local sources. The important criteria are to minimize local impacts in urban areas and, in rural areas, achieve broad spatial representation associated with secondary formation of aerosols and ozone that can be delineated from urban excess contributions.
  - leveraging with existing sites where practical, such as the speciation, air toxics and PAMS, and Clean Air Status (CASTNET) trends sites.
  - assuring consistency with collective criteria
  - consideration of other factors, such as resource allocation and level of Tribal participation.

#### 4.6.1.1 Broad-based Technical Guidance

Level 2 network design is initiated by first considering a cross-section of urban locations to support long-term objectives, such as epidemiological studies, then adding

rural locations to support the broad national objectives, including air quality modeling evaluation, emissions strategy accountability assessments, and trends/inter-regional comparisons. This is followed by a practical mapping of general locations with existing sites, and an equitable and objective allocation scheme. This sequential approach is captured in **Figure 4-2.** The top two segments of this figure represent, in general terms, the "needed sites," whereas the bottom two segments are examples of "existing sites." The intent is to maximize the existing site inventory in establishing Level 2 sites. (A complete set of existing network site location maps is contained in **Attachment 4.2.**)



**Figure 4-2.** National maps providing initial broad scale siting guidance for NCore level 2 sites. The maps include recommendations based on supporting long term health assessments (top left) that emphasize an aggregate of representative cities and air quality mode evaluations that rely on rural background and transport locations (top right). Existing site locations in most cases will be used as NCore siting infrastructure (bottom).

Nearly 80 "representative" air quality regions that group populations based on statistical and geographic factors form a cross-section of desired areas for long-term epidemiological studies. An additional 24 rural locations are identified to support evaluation of the national Community Modeling Air Quality System (CMAQ). These locations can be compared with available site candidates from existing networks (e.g., PM speciation, PAMS type 2 and CASTNET) that were designed with "representative" siting conditions commensurate with NCore Level 2 criteria. This procedure provides a modest objective-based reference to judge the adequacy of site allocation process.

#### **4.6.1.2 Site Allocation Process**

In determining how the Level 2 sites should be located, the NMSC felt that an initial proposal ought to consider nationwide equity and the fact that supporting grant funds to the States are not likely to change proportionally to support monitoring needs. Therefore, the initial allocation scheme, as summarized in **Table 4-2**, provides for a minimum of one Level 2 site per State. In addition, consideration for population is the basis for additional monitors, primarily, but not absolutely, in urban areas. Those States without population centers of at least 250,000 would be allocated rural-based Level 2 sites. Technical guidance sets a framework for assessing the development of NCore, while the allocation scheme provides a process for facilitating implementation. This allocation scheme is an initial proposal and generally provides a sweeping range of metropolitan areas. Clearly, allocation must be flexible enough to ensure that sites add meaningful value and avoid redundancies. Suspected shortcomings in the proposed allocation scheme that need to be reconciled include, for example, a lack of rural locations in California, lightly populated western States that may not provide a meaningful rural location, multiple Florida locations with generally moderate air quality due to marine influences, and possible redundant locations along the East Coast and Midwest.

Table 4-2. Proposed NCore Level 2 site allocations.					
	Total	Major Cities > 1M	Large Cities 500K - 1M	Medium Cities 250-500K	Rural
1 per State minimum	50				
3 each in most populated States (NY, CA, TX, FL)	8				
2 each in second tier populated States (OH, IL, PA, MI, NC)	5				
additional rural sites	10				
Total	74	32	13	11	18

NOTE: Allocation does not cover every major, large, medium sized city in the United States; States lack cities > 250,000 provide rural coverage.

#### **4.6.2** Level 1 and Level 3

NCore Level 1 sites are an important bridge for technology transfer and corroboration between research and regulatory oriented organizations. Because the resource prospects for supporting these sites appear limited at this point in time, as it is

not part of mainstream routine network, the determination of Level 1 sites will be undertaken when the funding prospects improve. As a guideline, however, these sites should include a range of representative locations across the Nation (e.g., allocating up to one site per EPA Region). Candidate locations could include existing supersites and other well-developed platforms capable of accommodating the space, power, and security needed for a large assortment of instruments. Consideration should be given to developing a rural-based Level 1 site to ensure that technologies tested today can meet future conditions as concentration levels continue to decline.

Level 3 sites retain several NAMS/SLAMS attributes. A large preponderance of Level 3 sites will be designated from the existing NAMS/SLAMS network. Some adjustments to existing networks are appropriate based on the network assessments, but those adjustments may involve re-locating existing monitors to better meet the Level 3 objectives.

#### 4.7. Site Selection and Approval Process

Except for Level 1 sites, it is envisioned that the selection of NCore sites will be undertaken by the host State/local agency or Tribe, but that review and approval will be done by EPA to assure that the recommended locations are consistent with the appropriate NCore site objectives. Since the Level 1 sites are considered the more research-oriented sites, and are dependent on additional funding, it is expected that EPA would take the lead in recommending appropriate Level 1 site locations. These can either be at existing Level 2 sites with adequate logistics to support a Level 1 effort, or an entirely new location. In either case, it would be expected that EPA would coordinate with the host State and/or local agency prior to finalizing the site.

Level 2 sites will be determined by the host agency or Tribe, and will require approval by the EPA Administrator. This approach insures that the collective national siting criteria are adhered to. It is expected that an NCore subcommittee of the larger NMSC will remain in place to assist EPA in assuring the appropriateness of the site locations.

Level 3 sites will be determined by the host agency or Tribe, and will require approval at the EPA Regional Administrator level. The regions are in the best position to understand the full complement of monitoring needs for the Level 3 site objectives, and therefore approval at the regional level is most appropriate.

The local-flexible portion of NCore, which is intended to meet local monitoring objectives, will not require EPA approval. However, SLTs, would be expected to notify EPA that such sites are being established.

#### 4.8 Relationship Between NCore and Existing Networks

Excluding CASTNET and IMPROVE, the existing State and local networks<sup>3</sup> largely consist of NAMS/SLAMS and special purpose/supplemental monitoring for criteria pollutants; PAMS; non-FRM portions of PM<sub>2.5</sub> network (e.g., speciation, supersites, and continuous mass); and air toxics. Most of these networks include a combination of prescriptive and less prescriptive monitoring based on relatively direct language in 40 CFR part 58 of the monitoring regulations, or through specific guidance in the Federal 103/105 Grants Program. The more prescriptive aspects include NAMS for all criteria pollutants, PM<sub>2.5</sub> SLAMS, PAMS, speciation trends, and the emerging air toxics national trends sites. Less prescriptive elements, not included in the monitoring regulations (i.e., "local-flexible" component), include special purpose/supplemental monitoring, SLAMS (other than PM mass), PM<sub>2.5</sub> speciation beyond trends, and a variety of air toxics sampling. Note that the estimated local fraction of resources for a particular program element is greatest for air toxics followed by PM<sub>2.5</sub> speciation. (See **Table 4-3**.) While much of the SLAMS monitoring for criteria pollutants is not required in 40 CFR part 58, over time, the monitoring has taken on a "required" context associated with various Clean Air Act requirements (e.g., design value sites, maintenance plan provisions, new source review, and miscellaneous arbitration).

	NCore	NCore <sup>1</sup>	NCore <sup>1</sup>	Local	Other	Notes
	Level 1	Level 2	Level 3			(All NCore sites support AIRNow)
PM Supersites	Т					lacking future funds
NAMS¹ (CO, NO2, O3, SO2, PM10, PM2.5)		Т				specified Level 2 PM2.5, PM10, NO/NOy do not use equivalent methods (assume each site has PM2.5 FRM; cont. PM10 and PM2.5 evolve into equivalent PM <sub>(10-2.5)</sub>
SLAMS <sup>1</sup>			Т			
PM speciation trends		Т			Т	assumes most (not all) trend sites are Level 2 locations
PM (SIP) speciation				Т		
Air toxic trends		Т				
Air toxics				Т		
PAMS type 2		Т		Т		unknown number of PAMS sites for Level 2
other PAMS				Т		

<sup>1 -</sup> Criteria pollutant trends are generated now from a subset of NAMS and SLAMS, and in the future from NCore Levels 2 and 3.

A rough comparison of NCore with existing networks suggests the following relationship:

- Level 1 = PM supersites
- Level 2 = criteria pollutant NAMS, speciation trends, air toxics trends, PAMS type-2
- Level 3 = SLAMS criteria pollutants

Several qualifying remarks are appropriate. The Supersites program is temporary and funding to transition into Level 1 master sites is not yet identified. Level 1 sites should be an integral long-term network component, and operate with greater intersite

consistency than the current Supersites. The minimum requirements determining criteria pollutant trends (analogous to NAMS), in most cases, would be accomplished through Level 2 sites. It is expected that the majority of speciation trend sites will be selected as Level 2 sites. The emerging national air toxics trend sites (NATTS) are being collocated at existing speciation sites, mostly trend sites, which in turn should emerge as formal NCore Level 2 sites. Approximately 50% of the remaining PAMS type-2 sites also serve as likely candidates for NCore level 2, and many of these already are collocated with speciation trend sites. Note that major fractions of air toxics, PAMS and PM speciation measurements are not part of NCore and should be viewed as part of the "local" network. However, agencies or Tribes supporting PAMS and PM speciation monitoring efforts would be strongly encouraged to integrate these into the Level 2 site structure, thereby providing greater multi-pollutant capabilities than the base Level 2 site.

### 4.8.1. Relationship to Existing PAMS, PM 2.5, Air Toxics, and NAMS/SLAMS Networks

The initial deployment phase of NCore relies on substantial leveraging from existing and emerging (e.g., air toxics) air monitoring networks. NCore would assume the "national" level or trend components of these programs. A more detailed discussion of these relationships is given below:

- Air Toxics Current discussions with the Air Toxics Steering Committee indicate a relatively small trends network with 10 to 20 sites established over the next 2 to 3 years covering a small group of hazardous air pollutants (HAPs) with "national" level importance (i.e., concentration predictions appearing in many places at levels of concern). More than 50% of the base air toxics monitoring resources would be dedicated to local needs. These trend sites could appropriately be located at Level 2 NCore sites.
- <u>PM2.5 Speciation</u> The speciation trends sites are excellent candidates to initiate siting locations for Level 2 multi-pollutant sites. The model established for the speciation program with approximately 50 national trends sites and nearly 200 SLT supplemental sites reflect the value associated with both local and national needs, and a blueprint for much of the development of NCore.
- PM<sub>2.5</sub> Mass Recent spatial analyses of these sites are forming an important tool for larger implementation issues associated with abating PM<sub>2.5</sub> levels throughout the United States. These sites will be assimilated into additional mapping tools such as AIRNow to provide forecasting and timely public access to AQI related information. The transition to continuous samplers, which requires a reduction in FRM samplers, is critically important. A substantial subset of PM<sub>2.5</sub> sites will be assimilated into the Level 3 sites.

• PAMS A side workgroup of the regulatory workgroup has developed a set of "minimum" PAMS recommendations. (See Table 4-4). The Type 2 PAMS sites included in this list of minimum requirements would be considered part of NCore. This revision was initiated in the January, 2000 PAMS workshop in Las Vegas and was based on redefining PAMS objectives. The PAMS principal objective now focuses on the longer term trends and accountability aspects, while playing a supporting role on other emissions strategy development objectives such as model evaluation.

MINIMUM REQUIRED PAMS MONITORING LOCATIONS AND FREQUENCIES			
Where Required	Sampling Frequency (All daily except for upper air meteorology) <sup>1</sup>		
Two sites per area, one of which must be a Type 2 Site.	During the PAMS season: 1) Hourly auto GC, or 2) Eight 3-hour canisters, or 3) 1 morning and 1 afternoon canister with a 3-hour or less averaging time plus Continuous Total Non-methane Hydrocarbon measurement.		
All Type 2 Sites	Hourly during the ozone season <sup>3</sup>		
One site per area at the Type 3 or Type 1 Site	Hourly during the ozone season		
One per Type 2 Site	Hourly during the ozone season		
All sites	Hourly during the ozone season		
All sites	Hourly during the ozone season		
One representative location within PAMS area	Sampling frequency must be approved as part of the PAMS Network Description described in 40 CFR 58.41.		
	FREQUENCIES  Where Required  Two sites per area, one of which must be a Type 2 Site.  All Type 2 Sites  One site per area at the Type 3 or Type 1 Site  One per Type 2 Site  All sites  All sites  One representative location		

<sup>&</sup>lt;sup>1</sup>Daily or with an approved alternative plan.

<u>NAMS/SLAMs</u> Components of the ozone sites in the current NAMS/SLAMS formulation will primarily be incorporated into the Level 3 adjunct sites for ozone.

<sup>&</sup>lt;sup>2</sup>Speciated VOC is defined in the Technical Guidance Document Reference \_, Target Compounds.

<sup>&</sup>lt;sup>3</sup>Approved ozone season as stipulated in 40CFR58, Reference --

#### 4.8.2. Linkage to Other Programs: Integration Beyond Traditional Networks

The clients of the SLT networks extend beyond the EPA Air Program Office and their immediate grantee organizations. For this Strategy to be truly national and sincere to optimization principles, there must be extended integration with other major networks and related national objectives. This integration should extend to:

- Global/continental air quality issues, including cross-continental transport of ozone, PM, and their precursors, persistent HAPs, such as mercury, dioxins, and PCBs, and to characterize global warming gases (e.g., ozone, carbon dioxide), and radiative losses due to light reflecting and absorbing aerosols and gases. In addition, intra-continental transport issues related to fluxes across U.S./Canadian and Mexican/U.S. borders should be served as part of the Strategy. Consideration should be given to an additional set of monitoring stations placed at critical locations along the coasts and borders for these purposes. Collaboration with other organizations, particularly NOAA, is suggested.
- Ecosystem and related assessments. Several national level monitoring efforts are in place or in planning potential for bidirectional benefits (i.e., two networks benefiting each other through complementary and/or similar measurements). Examples include CASTNET and IMPROVE, where both networks are used for routine evaluation of AQSMs, and visibility (IMPROVE) and atmospheric program (CASTNET) assessments, which benefit from SLT networks operating light scattering and chemical speciation measurements. Current planning for a routine PBT monitoring strategy focused on mercury, dioxins, and PCBs benefits from the existing networks through AQSM evaluation, as emerging models link across most pollutant categories, and mercury characterization is influenced by other species such as ozone. Advantages of leveraging operator resources and sharing platform space should be encouraged.
- Research and intensive field campaigns. Many of the more probing or diagnostic level research programs that attempt to uncover the underlying physical/chemical dynamics of atmospheric processes or characterize the more elusive or difficult specific causative factors responsible for adverse health effects are national needs. While these programs may primarily be conducted through research organizations and universities, it is imperative that they are perceived as integral components of the entire arsenal of technical tools used to understand, solve and account for progress in air quality management. As the Strategy is integrated more completely with other research level efforts, the efforts of routine monitoring operations will reap an important side benefit of additional counsel on routine aspects of monitoring operations, a process that has worked successfully to date with the Clean Air Scientific Advisory Committee (CASAC) Particle Monitoring Subcommittee.

The following are recommended and ongoing actions for extended integration to these three needs:

- Subject the Strategy, and specifically NCore recommendations, to broader scientific review and engagement with other Federal agencies and industry. Four specific actions include:
  - 1) establishing a new CASAC subcommittee to review NCore and related measurement methodology issues. This action was initiated in February 2002. This subcommittee will evaluate the NCore plan and provide counsel on the most reasonable mix of core pollutants, measurement locations, and related topics;
  - 2) adding NCore to the interagency discussions on air monitoring conducted under the Committee for Environment and Natural Resources (CENR) Air Quality Research Subcommittee (AQRS). This action was initiated in February, 2002;
  - 3) adding NCore as an integral component to the National Research Council (NRC) EPA PM coordination project that strives to facilitate coordination across modeling, monitoring and emissions and research and program objectives. This action begant in March, 2002
  - 4) adding Ncore to the NARSTO agenda to initaite dialogue with industry, Canada, Mexico, as well other NARSTO entities (e.g., states, EPA, universities). This action started in April, 2002 during the NARSTO Executive assembly meeting.
- Foster greater integration with networks such as IMPROVE and CASTNET by utilizing a subset those platforms as NCore rural sites. Several specific tasks that attempt to identify, characterize, and harmonize measurement differences between IMPROVE and the PM2.5 speciation network are underway through EPA studies by OAQPS, ORD and ORIA, and Regional Planning Organizations (RPOs) .IMPROVE monitors have been added to a subset of CASTNET sites thereby providing more integration across IMPROVE, CASTNET and PM2.5 speciation sites. The "core" Level 2 measurements should be added to some number of existing CASTNET and IMPROVE sites to enhance rural coverage.
- Collaborate directly with those organizations with the appropriate expertise and mission statements (e.g., NOAA) to build global and continental level monitoring needs into the national design.

#### 4.9. The Future of National Network Design

The NCore proposal presents a logical, yet inexpensive intermediate step toward implementing far more reaching and innovative approaches in monitoring. In reality, there are very few bold proposals in NCore, which really are more a series of necessary, pragmatic adjustments to our current networks. There must be an exploration of expanding the use of simplified and complex technologies into the system, including simple and inexpensive passive samplers that flood an area to fill important spatial gaps and support network design through evaluation of spatial analysis methods. Advanced optical technologies that characterize air quality over extended paths would be consistent with the emphasis on measuring "representative" air quality in response to national objectives. Can we do better than just "leveraging" existing networks and settling for a small number of comprehensive multi-pollutant sites? Or, should we build in a future design that is more directly need-based. How do we anticipate future needs? In one sense the NCore design is purposefully presented as a "minimum" to prevent stagnation and allow for accommodation of new needs and technologies.

The future vision for air monitoring should not be limited by the current state of knowledge and status quo. Rather, forward-thinking ideas, given the tremendous advancements in computers and micro-technologies, should be the foundation for future networks. The goal for air quality monitoring should be to provide the most comprehensive characterization of air quality over space (i.e., three dimensions), the time continuum, and physical/chemical properties. To reach that goal, the following principles should be associated with a more innovative future for air monitoring:

- 1. Multi-pollutant sites should be the standard rather than the exception. Air quality is complex and we need a far more comprehensive measurements approach to convey true ambient air characteristics.
- 2. New measurement technologies should be encouraged, developed, tested, and brought into the mainstream of monitoring network as quickly and effectively as possible. Recent examples include advances in miniature technologies that incorporate the near-equivalent of a continuous gas chromatograph housed on a microchip; the multiple chemical/physical (e.g., continuous aerosol chemistry and size characteristics) processing capabilities of single particle analyzers; the use of optical path instruments to sample representative volumes; and the expansion of remote satellite sensing capability.
- 3. Models and measurements need to be coupled dynamically to substantially improve our ability to guide air management programs. The geometric increases in computational capacity are now available to produce near-real-time output of predictive concentrations. This discussion on monitoring should be extended to incorporate modeling directly and in a manner analogous to the Four Dimensional Data Assimilation (FDDA) meteorological models where observed data

iteratively "nudge" predictive values closer to observations with the result being a detailed spatial output grounded on observations. The future of a system like AIRNow should evolve along the following lines:

- **current:** real-time view of ozone mapped data across most of the United States;
- **next 1- 5years** with NCore: real-time view of ozone and PM<sub>2.5</sub> mapped data and other Level 2 core pollutants at specific points;
- **next 5-10 years:** real-time view of complete spatial fields reflecting integrated observations/predictions for a list of pollutants outputted from models, combined with an analysis system integrating meteorological and satellite air quality data imagery with the capability of air quality forecasting over the entire nation.
- 4. Extend the current engineering design approach through a more idealized scientific approach, utilizing the outreach and integration and review process established (e.g., via CASAC, NARSTO, CENR). This will require an investment from, as well as to, the research community.

#### **4.10** NCore Implementation Schedule

The following schedule outlines the key time periods during which NCore is expected to be implemented.

#### 2002:

- Adjust NCore design, as appropriate based on public comment and scientific (e.g., CASAC) feedback
- Complete network assessments and recommendations for network changes to accommodate NCore design

#### 2003:

- Determine Level 2 site locations
- Establish Level 3 NCore sites
- Establish some Level 2 NCore sites

#### 2004-2005:

- Complete deployment of remaining Level 2 sites
- Establish and deploy Level 1 sites
- Complete development of future blueprint for "idealized" design and network structure
- Complete 3-year cycle local network assessments

#### 2005-2010:

- Evaluate and/or expand NCore as per idealized design and resource constraints
- Complete 5-year national network assessment

#### 4.11 Scientific Review

It is expected that there will be such a peer review, principally through the Clean Air Scientific Advisory Committee (CASAC) starting in Fall 2002. Additional input has been, and will continue to be, sought through numerous other opportunities, including: the Air Quality Research Subcommittee for Environment and Natural Resources, January 2002; NARTSO Executive Assembly Meeting, May 2002; PM Supersite Principal Investigator Meeting, June 2002; PM Health Centers Meeting, July 2002.

Initial review from EPA-ORD recognizes the national air monitoring networks as providing the critical long-term foundation to the scientific underpinning to both atmospheric sciences and health and exposure scientific research. These long-term monitoring networks have provided data to: support atmospheric dispersion and receptor type model development, evaluation, and application to help link or apportion pollution observed at a receptor back to its source; support NAAOS development; identify compliance and accountability, and support health and exposure studies. The scientific community supports the re-design of these networks from single pollutant purpose to multi-pollutant purpose, based on continuous monitors, that will address multiple objectives as described within this document. However, while this document represents an excellent beginning, there are still significant obstacles (resources – human and financial, and technology) that need to be overcome to fully meet the needs of the scientific community. However, this community also realizes that science is not the only objective of the proposed Strategy, that the obstacles are real and may not be able to be easily overcome in the near-term, and understands that these parameters might reduce the full usefulness of the data to the scientific community. A comprehensive review by different groups of scientists will of course maximize the cross link between the many objectives and further review by CASAC, NRC, and principal investigators of major air programs (e.g., Supersites Program, PM Health Centers) is strongly encouraged.

The scientific community will continue to provide recommendations and to interact with OAQPS and the States as details of the siting and measurements are refined. Specifically the health effects and exposure community are concerned with siting of both the multi-pollutant sites and removal of single pollutant sites that may have or will play key roles in future health studies. Atmospheric scientists and air quality modelers are interested in continued communications to further support the siting of regional and rural as well as urban site locations to further support work across the source-receptor-exposure paradigm. Sufficient resources are needed to maximize the usefulness of the re-designed networks across all objectives realizing that the limited number of sites is close to but not quit sufficient to meet the multiple needs of this strategy. Specific details

of where additional resources are needed will be discussed through the review process. Finally, there is a critical need to fund the Level 1 sites that will provide long-term chemical and physical data about given geographical areas that cannot be obtained at more than a few (8-10) sites nationwide. The scientific community believes this is a critical area need and that their involvement is essential to the development of this part of the network.

#### **4.12 Resource Implications**

The working assumptions for NCore are based on protecting and even enhancing the degree of flexibility SLTs have in conducting monitoring to meet their identified needs. It is anticipated that there are some very moderate resources to be allocated to NCore that will emerge from the network assessments that indicate reductions of traditional criteria pollutant monitoring sites. The development of NCore will also capitalize on resources available for special programs, such as PAMS and PM<sub>2.5</sub> speciation. It is further anticipated, though, that certain components of NCore will need additional funding initiatives because the divestment from existing programs is not sufficient to completely meet all the investment needs. Therefore, two very important implementation tasks need to be followed. First, as described above, maximum leveraging and optimization of existing networks must drive the initial implementation of NCore over the next one to five years. This includes strong encouragement, or perhaps requirement through regulations, to integrate the new air toxics trend sites into NCore. Second, modest investments from EPA must be contributed to catalyze NCore. Those costs, which are expected to be covered by network adjustment resource savings, include the establishment, operation, and maintenance of all Level 2 and Level 3 sites (with the exception of new equipment capital costs), and all local/flexible sites.

Those costs, for which additional targeted resources are needed, have not been fully defined, but are estimated in the following list:

#### Level 2 enhancements

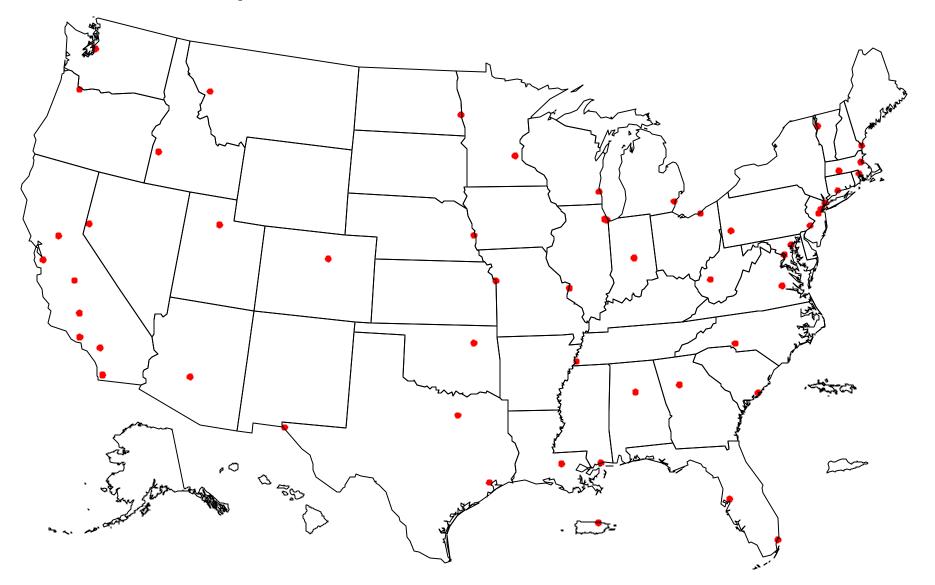
- 1. Purchase of equipment (including supporting QC calibration systems):
  - ! High-sensitivity CO, SO<sub>2</sub> and NO/NOy instruments (\$5 million)
  - ! Continuous PM instruments (\$2 million)
- 2. Monitoring platform enhancements (e.g., space, power) (\$2 million)
- 3. Installation of information transfer technology hardware and software and data base expansion and incorporation of continuous Level 2 and Level 3 data into AIRNow. (\$2 million).

#### Level 1

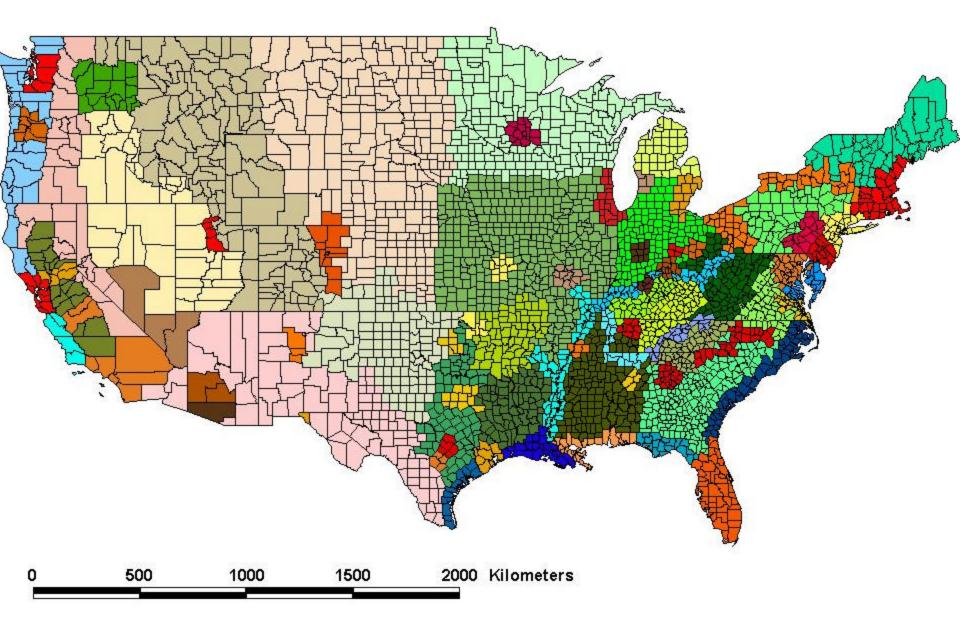
Level 1 sites are an integral component of NCore that strongly reflects the themes of insightful measurements and new technologies underlying the Strategy. Unfortunately, currently there appears to be no clear funding source to support these "transitional" sites, as standard resource pools historically have been associated with routine operations (e.g., Federal 103 and 105 Grants) or relatively open-ended research Grants to Universities for new methods development and testing. Clearly, strong consensus support must be developed for Level 1 sites to drive a funding initiative. It is premature to detail a cost proposal for Level 1 sites as the scope of operations is very loosely defined. For budget estimation needs, we will assume that a minimum of \$2-3M per year is required for Level 1 operations and analysis as well as an initial \$4M in capital expenses.

Thus the total additional costs to implement NCore are estimated at \$15 million, one-time expense; and \$2 million recurring annual operating expenses (Level 1).

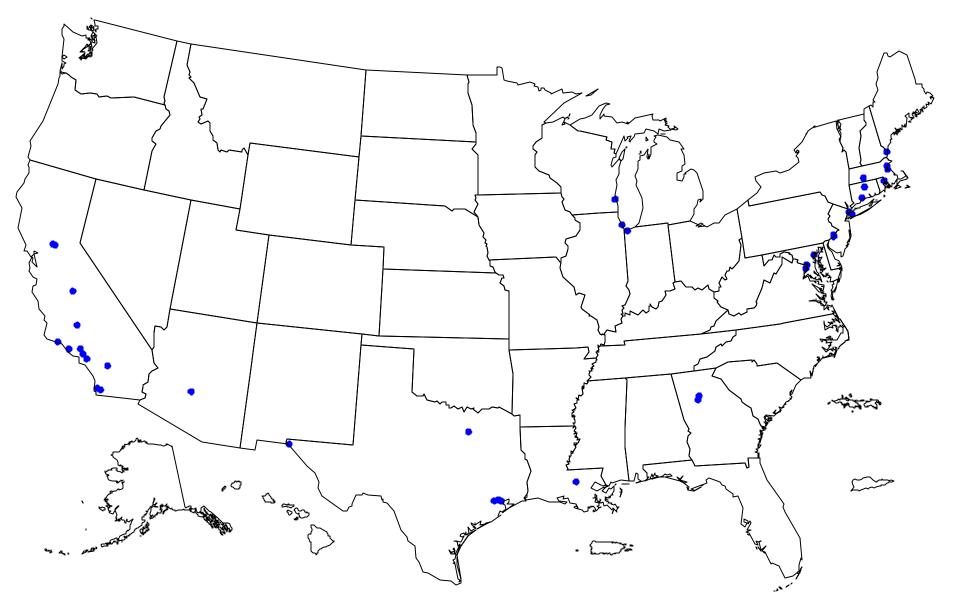
## Speciation 'Trends' Sites



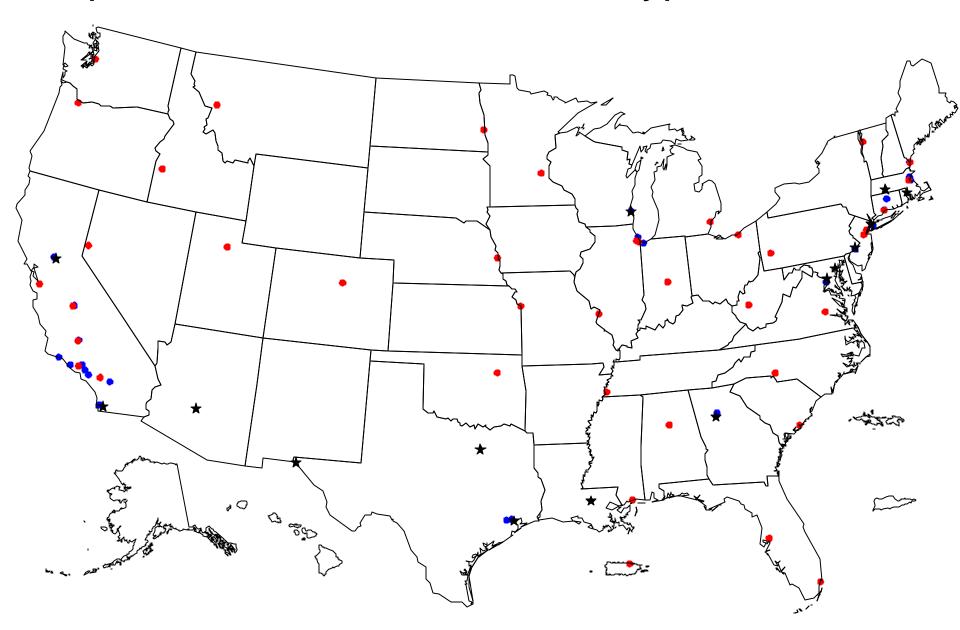
## Figure 1: Population-based Air Quality Regions



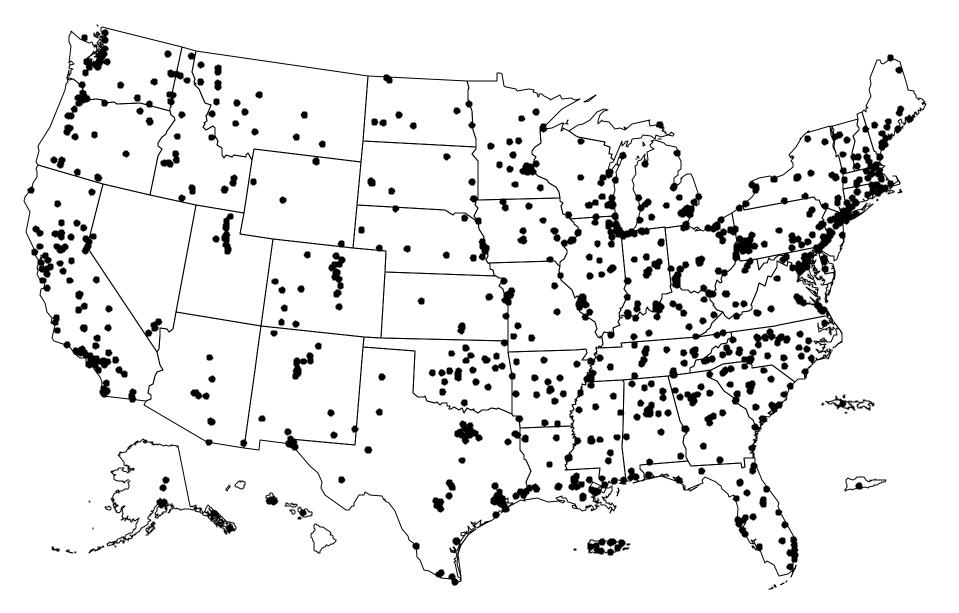
## PAMS 'Type 2' Sites



## Speciation 'Trends' & PAMS 'Type 2' Sites



### PM<sub>2.5</sub> Sites



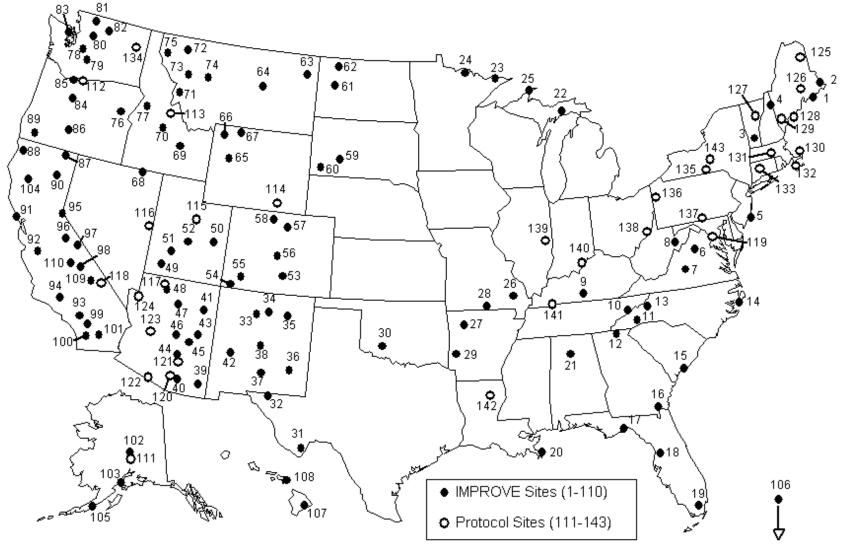
### Ozone Sites



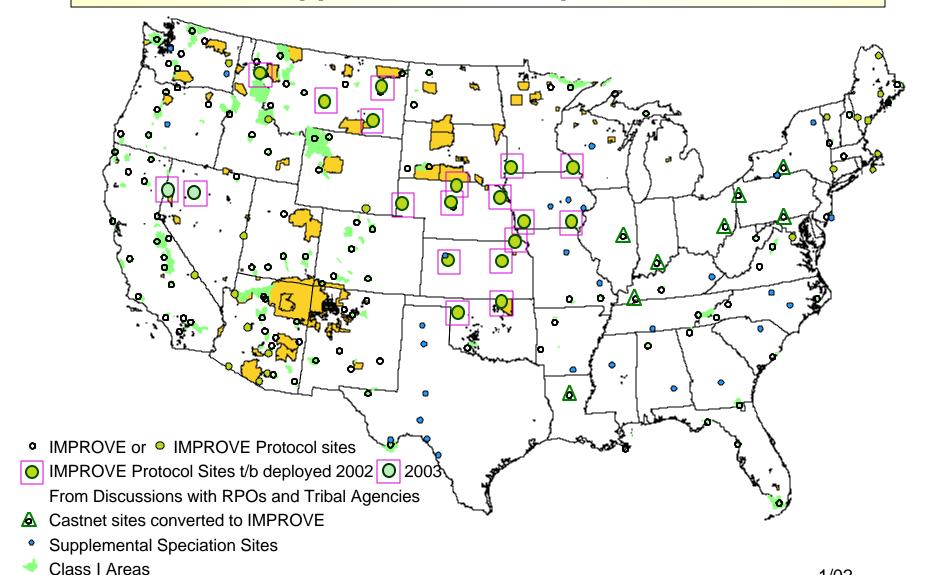
### **CASTNet Sites**



## IMPROVE (rural sites)



# Current/Planned IMPROVE, IMPROVE Protocol & Rural Supplemental PM<sub>2.5</sub> Speciation Sites



1/02

Tribal Lands

### Air Quality Monitoring in Support of Epidemiology

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ORD / NHEERL / HSD / EBB

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#### Air Quality Monitoring in Support of Epidemiology

Epidemiologic studies of the health effects of ambient particulate matter have been enormously important in determining the real health effects of real-world exposures to ambient particulate matter and co-pollutants among real human populations with the relevant range of variations in sensitivity. While some studies have generated their own air quality monitoring data, many epidemiologic studies have relied entirely on routinely collected air quality data supplied by a compliance-oriented air quality monitoring system. The health-based nature of the current air quality standards for particulate matter suggest a strengthening of this link between epidemiologic studies and compliance-oriented air quality monitoring systems.

By analogy, police officers are required to do more than simply find and arrest the bad guys. Police officers are expected to be on the watch for hazardous situations, such as adverse road conditions (exposure assessment); to assist citizens by summoning emergency services (health assessment); and to be particularly active in situations where these two conditions coincide, such as a hurricane warning (risk assessment and communication). Compliance-oriented air quality monitoring systems should also be designed to maximize their utility for these ancillary functions.

The choices involved in the determination of routine air quality monitoring systems will have important consequences for future epidemiologic research, for future risk assessments and for future regulation. The early choice of a 2.5 micron cut-point for fine particulate matter by research scientists has had important and unforeseen consequences for the air quality standard. The decisions now being made regarding compliance-oriented air quality monitoring systems will shape future epidemiologic research. For example, if the proposed air quality monitoring system cannot distinguish between the source contributions of gasoline and diesel vehicles, then many future epidemiologic studies will not be capable of making any distinction between these sources.

#### **Types of Epidemiologic Studies**

Various non-epidemiologists have complained about the inability of epidemiologists to clearly indicate their needs for air quality monitoring systems. Each epidemiologist seems to be describing an entire different set of research requirements. This apparent lack of consensus among epidemiologists is primarily a reflection of the differing exposure assessment requirements of different epidemiologic study types.

Epidemiologic studies of the health effects of ambient particulate matter fall into several distinct study types. Each type of study requires air quality data over different frequencies of measurement, different durations of measurement, different levels of geographic scope, and different levels of geographic detail. These epidemiologic studies fall into four broad categories: unenumerated open-cohorts ("time-series studies"), prospective closed-cohorts with repeated measurements, closed-cohorts analyzed for the timing of a health event ("case-crossover studies") and closed-cohorts analyzed for survival.

#### **Unenumerated open-cohorts**

Epidemiologic studies of unenumerated open-cohorts have played a key role in identifying fine particulate matter as an important public health problem. Since mortality and hospitalization records are routinely collected by public health authorities, these studies only require the addition of routinely collected daily data on weather and on ambient concentrations of particulate matter and co-pollutants. These studies have been conducted throughout the world under a large number of climatic conditions and sources of particulate matter.

The sample size of these studies is generally one or more well-defined urban areas each with a population of 100,000 or more persons followed over years of daily observations. While early studies

were limited to single cities, the most extensive study was Jon Samet and colleagues' analysis of 90 U.S. cities (1). These 90 cities covered a broad range of city sizes: 3 cities were over 5 million, 20 cities were between 1 and 5 million, 35 cities were between ½ and 1 million, and 32 cities were under ½ million population. With the increase in the number of cities considered in a single study, researchers have gained an ability to examine the determinants of city-to-city variability in the exposure-response relationship.

The <u>frequency</u> of air quality measurements required for these studies depends on the time resolution of the health data. Since mortality and hospitalization data is available as daily counts, the ambient air quality measurements should be conducted at least daily at fixed locations with a minimum of missing data. The timing of missing air quality values must not be related to both air quality levels and health effects. Even routine one-in-six or one-in-three day sampling introduces an unacceptable pattern of missing values into the data and severely limits the analysis of the delayed (or lagged) health effects of particulate matter.

The <u>duration</u> of air quality measurements required for these studies depends on the size of the observed population and the natural variability of air quality levels. For most populations in a single urban area, air quality measurements must be continued for extensive periods of time (years or decades) in order to gain sufficient statistical power in terms of person-time of observation. However, a national network of monitoring stations representing the exposures of large numbers of individuals combined with daily source apportionment might be able to generate annual reports on the relative toxicity of different sources of particulate matter.

The <u>geographic scope</u> of air quality measurements required for these studies depends on the geographic scope of the health data system. While the scope of a hospital-based record system is limited by the size of the individual hospital's catchment area, mortality records and federally-assisted hospital care

records are national in scope. A more extensive air quality monitoring network will (a) increase the total size of the population under study, (b) increase the number of study cities, (c) increase the statistical power to detect the relative health effects of various pollutants, (d) increase the ability of the study to understand the effects of various combination, and (e) increase the ability of the study to examine effect modifiers such as personal characteristics, behaviors, and situations, such as age, preexisting conditions, smoking status, and air conditioning. A nation-wide air quality monitoring system that captures the day-to-day variability in air quality levels for the entire U.S. population would permit an extension of these studies.

The geographic detail of air quality measurements required for these studies depends on the small-scale spacial variability of the pollutant under study and the geographic detail of the health data. Due to privacy concerns, health data are generally not available at less than the county or city level. Fortunately for these studies, the exposure data do not need to reflect the mean exposure of specific individuals or their total exposures to ambient and non-ambient particulate matter. The exposure data must only capture the day-to-day variability in ambient air quality levels for the population as a whole. Methodological issues concerning the use of a single central-site monitor to represent the exposures to particulate matter over broad geographic areas have been largely resolved by recent exposure assessment research.

#### **Prospective closed-cohorts with repeated measurements**

Epidemiologic studies of prospective closed-cohorts with repeated measurements of symptoms and physiological parameters ("panel studies") in both field and clinical settings have been instrumental in developing our understanding of the biologically plausible modes of action for particulate matter. By allowing each subject to serve as their own control, these studies have considerable statistical power to detect the determinants of the day-to-day variability of health. The physiological parameters have included

pulmonary function (2), heart rate and heart rate variability (3), and biomarkers such as fibrinogen, C-reactive protein and plasma viscosity (4).

The sample sizes of these studies are generally of the order of 60 people followed three times each week for four- week periods, but a recent German study followed about 60 people monthly for an entire year. In the U.S., these studies tend to be of limited duration due to the costs of repeated measurements and subject boredom. However, both the National Cooperative Inner-City Asthma Study and the subsequent Inner-City Asthma Study used an interesting variant of this study design with rotating panels of study subjects each of whom were on study daily for two week periods spaced at six-month intervals (5). By dividing their subjects into 12 groups, the investigators were able to maintain a study of children under observation daily for 18 months.

The <u>frequency</u> of air quality measurements required for these studies depends on the time resolution of the health data. Since the timing of the health measurements is often under the control of the investigator, these studies have investigated the health effects of exposures one to four hours prior to the health examination. Continuous or hourly data on air quality will be of great utility to these studies.

The <u>duration</u> of air quality measurements required for these studies depends on the period of observation of the health effects. In most studies involving intensive physiologic measurements, the duration of observation is relatively brief, four to eight weeks. For the rotating panel design, the period of health observation was over 18 months. The air quality monitoring system should not be reduced in frequency or geographic detail during such studies.

The <u>geographic scope</u> of air quality measurements required for these studies depends on the geographic scope of the study population. These epidemiologic studies are general conducted with health

measurements performed at a single location, but successful studies have been conducted with subjects scattered over a single community. As with the open-cohort studies, the exposure data must capture the short-term variability in air quality levels for the study population as a whole. The exposure data do not need to reflect the mean exposure of any individual or the total exposures to ambient and non-ambient particulate matter.

The geographic detail of air quality measurements required for these studies depends on the small-scale spacial variability of the pollutant under study. For pollutants with low small-scale variability, such as fine particulate matter, central site measurements generally are sufficient, while for pollutants with considerable small-scale variability, such as ultrafine particulate matter, air quality measurements should be conducted near to the location where the health measurements are performed or where the study subjects reside.

#### Closed-cohorts with timing of a health event

Epidemiologic studies of closed-cohorts based on the timing of a health event are generally distinguished from the prospective cohorts with repeated measures in that either a) the subjects are identified by the occurrence of a rare health event such as a myocardial infarction (6) or b) the health data is generated by the recording of a rare health event such as the discharge of an implanted cardiac device (7). In both cases, the analysis concerns the exact timing of the health event and proceeds using a case-crossover method.

While only a few epidemiologic studies have been conducted using this study design, the research potential of such studies is great. The clinical significance of either a myocardial infarct or a device discharge is obvious. Given that these are rare health events, these studies are generally conducted in a

retrospective manner with the acquisition of exposure data from a routine monitoring system after the occurrence of the health event.

The <u>frequency</u> of air quality measurements for these studies depends on the time resolution of the health data which can be quite precise when recorded by an implanted cardiac device. While routine hospital data does not have sufficient time resolution, recent studies have relied on interviews with heart attack survivors to establish the timing of the onset of symptoms. Due to the significance of the cardiac event and the important of prompt care, the timing of the onset of symptoms is often well remembered by the survivor. Continuous or hourly data on air quality will be of great utility to these studies.

The <u>duration</u> of air quality measurements required for these studies depends on the need to collect a sufficient number of health events for analysis. Since the required time period can easily cover several years, a stable air quality monitoring system that can provide extensive historic data will greatly facilitate these studies.

The geographic scope of air quality measurements required for these studies depends on the geographic scope of the study population. While these studies generally are conducted in a few hospitals or a single clinical practice, the study subjects may come from relative large catchment areas encompassing entire urban areas. As with the open-cohort studies, the exposure data must capture the short-term variability in air quality levels for the study population as a whole. The exposure data do not need to reflect the mean exposure of any individual or the total exposures to ambient and non-ambient particulate matter.

The <u>geographic detail</u> of air quality measurements required for these studies depends on the small-scale spacial variability of the pollutant under study. For pollutants with low small-scale variability, such

as fine particulate matter, central site measurements generally are sufficient. However, a recent study found that cardiac events were more strongly associated with nitrogen dioxide than with fine particles (7). This finding suggests that pollutants with greater small-scale variability, such as ultrafine particulate matter, may be producing this health effect. Furthermore, these studies should be capable of ascertaining the location of each study subject at the time of the event which would permit the use of very fine geographic detail on air quality.

### **Closed-cohorts analyzed for cumulative incidence (survival)**

Epidemiologic studies of closed-cohorts analyzed for cumulative incidence of a health event over time have shown the most adverse effects of long-term exposures to particulate matter. In adult cohorts, these studies follow the survival of a well-characterized cohort of subjects in communities with differing long-term air quality exposures. In cross-sectional studies of children, these studies collect information on children's health status during the time preceding the survey.

The two major adult survival studies have been the Dockery and colleagues study of 8,111 adults followed for 14 to 16 years in six U.S. cities (8) and the Pope and colleagues study in 151 U.S. cities using the American Cancer Society cohort of 552,138 adults followed for nine years (9). While Dockery and colleagues' study in six U.S. cities was supported with research-oriented air quality monitoring, the Pope and colleague's study relied entirely on routine compliance-oriented air quality monitoring. Follow-up of these cohorts has continued through 2000 and will be continued as these cohorts advance in age.

Examples of the many children's cohorts include Harvard Six-Cities Studies (10), the Harvard 24-Cities Studies (11, 12), the Kanawha Valley Health Study (13), and the Southern California Children's Health Study (14, 15). The Harvard studies dealt with large-scale differences on long-term exposures

across different communities, while the other two studies dealt with intra-urban gradients of air pollutants. In all cases, limited air quality monitoring was used to infer long-term exposure histories for these children.

The <u>frequency</u> of air quality measurements required for these studies are less intensive than for the other study types. Monthly averages should be sufficient for this type of study, so long as the measurements are sufficiently frequent to capture the average ambient air quality during the month. One-in-three day air quality monitoring may be sufficient, but one-in-six day monitoring may not be adequate for the calculation of monthly averages.

The <u>duration</u> of air quality measurements required for these studies is considerably more extensive than for the other study types. In order to adequately capture the long-term exposure history of study subjects, the air quality monitoring data must capture a considerable portion of their lifetime. The nine to 16 years of follow-up in the cited studies still required the assumption that the relative rankings of the cities with respect to air quality during the follow-up period correctly represented the relative rankings of long-term exposures for the subjects.

The geographic scope of air quality measurements required for these studies is also greater than for the other study types. Due to the high geographic mobility of the U.S. population, a single location cannot adequately represent many individuals' long-termexposures. A nation-wide air quality monitoring network that captures the ambient air quality exposures of a substantial portion of the U.S. population would be necessary for these studies.

The geographic detail of air quality measurements required for these studies needs to adequately characterize individuals' long-term exposures to ambient pollutants. Since healthy adults tend to travel around within their local communities, intra-community geographic detail may be less important for this type

of study. However, given the broad, national scope proposed for such a study, regional geographic detail is very important. Increased geographic detail may be required for communities with local heavy industry and within a complex urban setting such as the U.S. Eastern Megalopolis. The most important requirement for this type of study is that the exposure assessment methods must be standardized across all monitoring locations. Variations in monitoring methods could result in false associations between health and air quality.

## Epidemiologic study requirements for air quality monitoring

The requirements for air quality monitoring differ greatly across the various epidemiologic study designs (table 1). This table clarifies the differing requirements expressed by epidemiologists for routine air quality monitoring systems. The exposure assessment requirements for epidemiologic studies differ greatly according to the type of studies under consideration.

Table 1. Summary of air quality monitoring requirements by type of epidemiologic study.				
	Unenumerated Open-Cohorts	Closed-Cohorts with repeated measures	Closed-Cohorts analyzed for event timing	Closed-Cohorts analyzed for cumulative incidence
Frequency	Daily	Hourly	Hourly	Monthly
Duration	Years to Decades	Weeks to Years	Years	Decades
Geo. Scope	Urban Centers	Limited	Urban Centers	U.S. Population
Geo. Detail	County	Study site	County	Regions

The maximum requirements for a comprehensive air quality monitoring system are clearly quite daunting: hourly data collected for decades to capture both the short-term and long-term exposures of populations ranging from a few study subjects to the U.S. population as a whole and from regional to neighborhood levels of detail.

Compliance-oriented air quality monitoring systems alone cannot fully meet the needs of epidemiologic studies. Research-oriented air quality monitoring and air quality models will be required to supplement the compliance-oriented systems. However, research-oriented air quality monitoring is an expensive and difficult component of prospective epidemiologic research. Epidemiologic research on the long-term exposures of adults requires the assessment of exposures over decades with a real premium on routine and geographically extensive compliance-oriented air quality monitoring systems.

### Combination of monitoring and modeling

Environmental epidemiologists are accustomed to using limited environmental measurements in the context of a model. Often these models are very naive and simplistic, such as assuming that central site monitoring can well capture the ambient exposures of an extended population over a wide geographic area and that measurements conducted over limited periods can adequately capture past exposure gradients. Nevertheless, epidemiologic studies utilizing these simple models have been very successful in elucidating the health effects of environmental exposures. More sophisticated models have not always shown a clear advantage in statistical power over the simpler models, since model precision often comes at substantial cost and a reduced sample size. However, by using appropriate air quality models and geographic information systems, a compliance-oriented air quality monitoring system with limited direct measurements could be used to provide more intensive research data.

The <u>frequency</u> and <u>geographic detail</u> do not need to be the same for each air quality monitoring parameter. Since many parameters are highly correlated, air quality models may allow the imputation of values across different levels of frequency and geographic detail. For example, a temporal air quality model could permit the pairing of (a) a device measuring hourly light scattering or beta-emission attenuation that

provides a high-frequency estimate of PM<sub>2.5</sub> with (b) a lower-frequency (24-hour), but more accurate gravimetric measurement of PM<sub>2.5</sub>. Similarly, a spatial air quality model could permit the imputation of exposures to ultra-fine particulate matter from (a) costly ultra-fine measurements at a few locations, (b) co-pollutants measured at more locations with greater geographic detail, and (c) distance to and traffic density on nearby roadways. Spatial air quality models may also permit measurements of specific pollutants conducted at differing locations to be integrated into a common model.

The interaction between geographic scope and geographic detail is particularly relevant for the assessment of long-term exposures. A nation-wide system for exposure assessment (scope) will require the identification of a sufficiently large number of geographic regions so that long-term average air quality levels are relatively uniform across the area (detail). An illustrative attempt at the delineation of population regions across the U.S. is included as Appendix A. For some study designs, these regional averages could be supplemented by information on the subject's residential location with the study region.

Geographic information systems have great potential for application to these problems. In principle, the residential location of most study subjects may be ascertained to specific street addresses which may be mapped to census and traffic engineering data. Data from the U.S. Decennial Census can provide information on neighborhood characteristics including population density and type of housing. Routinely collected traffic engineering data can provide the location of major highways and traffic density for most urban areas. In addition to this information on these mobile and area sources, the locations and emissions of point sources would complete the source profile. The locations of and data from compliance-oriented air quality monitoring stations would complete the geographic information system.

The precision required for a national air quality exposure assessment system should be defined in terms of the relative error for specific proportions of the U.S. population. A small proportion (less than 1 percent) of the study population could have their exposures greatly misclassified (greater than 20 percent) without introducing a important bias into an epidemiologic study, provided that the exposure misclassification was unrelated to their health status after adjustment for age and other measurable characteristics.

### **Conclusions**

Compliance-oriented air quality monitoring has played and will continue to play a major role in determining the ability of epidemiologists to assess the health effects of ambient pollutants. Any new system should be national in scope with carefully standardized measurements, with an ability to provide hourly data and monthly averages, and with sufficient geographic detail to permit accurate community-level exposure estimates. The monitoring system must be coupled with a research-oriented modeling system that will permit increased time and spatial resolution for less frequent and more widely spaced monitors.

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# **Air Quality Monitoring in Support of Epidemiology**

# Appendix A:

**Population-based Air Quality Regions** 

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### Appendix A: Population-based Air Quality Regions

The 281,421,906 residents of the United States (April 1, 2000) are unevenly spread over an area of 9,628,382 square kilometers (km²) divided by civil jurisdictions into 3,111 counties and equivalent entities. No air quality monitoring network can fully capture the ambient air concentrations of criteria air pollutants in the vicinity of their 105,480,101 occupied housing units. This problem of air quality exposure assessment for the U.S. population can be reduced to a more manageable scope by a geographic information system that combines direct monitoring at a comprehensive network of air quality monitoring stations with sophisticated models. As an aid to this process, the entire area of the U.S. must be divided into a limited number of smaller, more tractable air quality regions. This document is an initial attempt at a population-based approach to the designation of air quality regions.

The densest concentrations of the U.S. population are found in 253 Metropolitan Statistical Areas (MSA) and 19 Consolidated Metropolitan Statistical Areas (CMSA) designated and maintained by the White House Office of Management and Budget (OMB) in the Federal Information Processing Standard (FIPS) 8-6. The 19 CMSA's are divided into 76 Primary Metropolitan Statistical Areas (PMSA). These MSA's/CMSA's range in population from the 21,119,865 residents of the New York–Northern New Jersey–Long Island, NY–NJ–CT–PA CMSA to the 57,813 residents of the Enid, OK MSA and contain 81 percent of the U.S. resident population. The MSA's and the non-metropolitan counties and equivalent entities form the elemental units of the designated air quality regions. In several policy statements, OMB has indicated that all Federal Agencies should utilize these MSA's. These designated air quality regions are therefore aggregates of well-defined statistical entities.

For the purposes of designating air quality regions, this process of aggregation from MSA's does lead to certain unusual features on a map. For example, the county of San Bernardino, CA is part of the Los Angeles–Riverside–Orange County, CA CMSA even though much of the county's area lies east of the Sierra Nevada mountains. The central point for the weighted population distribution within San Bernardino (the population centroid) lies near the western edge of the county. The overwhelming majority of the residents of San Bernardino county are properly characterized by their inclusion in the Los Angeles–Riverside–Orange County, CA CMSA.

The current version of these air quality regions (figure 1) does not cover Alaska (626,932 residents) or Hawaii (1,211,537 residents). The Commonwealth of Puerto Rico is not included in the U.S. population totals or in the current air quality regions. In future versions, Alaska probably should be divided into two or more air quality regions, while Hawaii and Puerto Rico probably should be single air quality regions.

### **Air Quality Considerations**

These population-based air quality regions have been assembled with a basic knowledge of the general determinants and levels of criteria air pollutants, but not on the basis of specific air quality measurements. In each region, air quality sources will be a combination of (a) the long-range transport of primary and second pollutants, (b) the atmospheric generation of secondary pollutants from transported and locally-generated primary pollutants, (c) area sources, (d) local mobile sources, and (e) local point sources. The first two source categories will result in regional-scale increases in air pollutant concentrations, while population-exposures to air pollutants from the other three source categories may be more greatly affected by proximity to the source.

Ideally, each air quality region should be small enough so that the region's population experiences similar exposures to the regional-scale sources of air pollution. However, considerable variations may still exist in population exposures to air pollutants from local sources. Air quality regions that would be small enough to ensure complete uniformity of population exposures to pollutants from all sources would be too numerous to permit the development of a workable exposure assessment system.

The exposure of the air quality region's residents to regional-scale exposures to air pollutants may be determined from direct monitoring. The determination of population exposures to local sources, such as mobile sources, will require a combination of direct monitoring and modeling. The air quality models will need to take into consideration each resident's proximity to major roadways, the density and type of traffic on these roadways, and the density of smaller roadways in the neighborhood. These small-scale

considerations may be more important in air quality regions with considerable variation in the density of population, housing units, and roadways.

### Types of Air Quality Regions

The 23 major urban regions consist of one or more undivided MSA's or CMSA's. These major urban areas range in size from the 21,104,292 residents of the New York City air quality region to the 2,566,053 residents of the Richmond to Norfolk air quality region. In a few instances, one or more adjoining non-MSA counties have been included to preserve the contiguous nature of these major urban areas. The combined populations of these 23 major urban regions (139,682,947 residents) is nearly half of the entire U.S. population.

The 21 **city regions** consist of MSA's with populations between 750,000 and 2,500,000 residents that are not part of larger urban areas. A few of the small MSA's within the following rural regions may deserve promotion to city areas if local conditions warrant their increased monitoring. An example of such a city is the El Paso, TX MSA that is located just north of the major Mexican city of Ciudad Juarez (over 2,000,000 residents). The combined populations of these 21 city regions (23,392,084 residents) is eight percent of the U.S. population.

The 17 **rural regions** consist of less urban counties and equivalent entities, but may include isolated MSA's of less than 750,000 residents. The designation of these rural regions followed to general boundaries of the State Economic Areas delineated by the U.S. Bureau of the Census in the 1950's. The Appalachian rural regions follow the boundaries established by the Appalachian Regional Commission, but

this region was divided into five air quality regions to allow for regional-scale differences in air pollutant concentrations. These rural regions contain small MSA's which are listed in the definition of each region.

The 4 **valley regions** consist of rural regions along major waterways in the eastern U.S. Historically, narrow river valleys have been a major factor in locally high air pollutant concentrations and in major air pollution disasters such as occurred in Denora, PA. These valley regions may include isolated MSA's of less than 1,000,000 residents.

The 7 **coastal regions** consist of counties within 10 km of the coast lines of the U.S. and outside the major urban areas. Unlikely narrow river valleys, coastal regions have generally low air pollutant concentrations due to on and off shore breezes and other routine meteorological conditions. The major urban areas of the northeastern U.S., Houston, TX and Pensacola to New Orleans are not included as coastal regions.

The 7 **extremely low-density regions** consist of rural regions with population densities less than 7 residents per km<sup>2</sup>. Due to the low population density, air quality monitoring is a very inefficient means of estimating population exposures. Fortunately, air pollutant concentrations tend to be very low in these regions. Only four of the MSA's in these low-density regions have more than 240,000 residents: the Albuquerque, NM MSA (712,738 residents); the Boise City, ID MSA (432,345 residents); the Reno, NV MSA (339,486 residents); and the Lubbock, TX MSA (242,628 residents).

# Major Urban Regions

The **New York City** air quality region (21,104,292 residents) consists of the New York–Northern New Jersey–Long Island, NY–NJ–CT–PA CMSA excluding Litchfield county, CT (26,829 km² with 787 residents per km²). This CMSA includes the following 15 PMSA's: Trenton, NJ (350,761 residents); Bergen–Passaic, NJ (1,373,167 residents); Jersey City, NJ (608,975 residents); Middlesex–Somerset–Hunterdon, NJ (1,169,641 residents); Monmouth–Ocean, NJ (1,126,217 residents); Newark, NJ (2,032,989 residents); New York, NY (9,314,235 residents); Newburgh, NY–PA (387,669 residents); Dutchess County, NY (280,150 residents); Nassau–Suffolk, NY (2,753,913 residents); New Haven–Meriden, CT (542,149 residents); Stamford–Norwalk, CT (353,556 residents); Bridgeport, CT (459,479 residents); Danbury, CT (183,303 residents in Fairfield county); and Waterbury, CT (187,200 residents in New Haven county). In order to preserve county boundaries in the New England area, this regiondoes not include any portion of Litchfield county, CT: 34,677 residents of the Danbury, CT MSA and 41,784 residents of the Waterbury, CT MSA.

The **Washington/Baltimore** air quality region (7,608,070 residents) consists of the Washington–Baltimore, DC–MD–VA–WV CMSA (24,825 km<sup>2</sup> with 307 residents per km<sup>2</sup>). This CMSA includes the Baltimore, MD PMSA (2,552,994 residents), the Washington, DC–MD–VA–WV PMSA (4,923,153 residents) and the Hagerstown, MD PMSA (131,923 residents).

The **Philadelphia** air quality region (6,188,463 residents) consists of the Philadelphia–Wilmington–Atlantic City, PA–NJ–DE–MD CMSA (15,483 km² with 400 residents per km²). This CMSA includes the Atlantic–Cape May, NJ PMSA (354,878 residents), the Philadelphia, PA–NJ PMSA (5,100,931 residents), the Vineland–Millville–Bridgeton, NJ PMSA (146,438 residents), and the Wilmington–Newark, DE–MD, PMSA (586,216 residents).

The Boston/Providence/Hartford air quality region (10,320,465 residents) consists of 31 counties along the Atlantic coast from Hartford, CT to Portland, ME (43,225 km<sup>2</sup> with 239 residents km<sup>2</sup>) including the Boston-Worcester-Lawrence, MA-NH-ME-CT CMSA. The Boston–Worcester–Lawrence, MA–NH–ME–CT CMSA includes the following 10 PMSA's: Boston, MA-NH (3,406,829 residents); Brockton, MA (255,459 residents); Fitchburg-Leominster, MA (142,284 residents); Lawrence, MA-NH (396,230 residents); Lowell, MA-NH (301,686 residents); Manchester, NH (198,378 residents); Nashua, NH (190,949 residents); New Bedford, MA (175,198 residents); Portsmouth–Rochester, NH–ME (240,698 residents); and Worcester, MA–CT (511,389 residents). Six smaller MSA's that lie north of the New York City region have been joined into this air quality region including the Providence-Fall River-Warwick, RI-MA MSA (1,188,613 residents), the Hartford, CT MSA (1,183,110 residents), the New London-Norwich, CT-RI MSA (293,566 residents), the Springfield, MAMSA (591,932 residents), the Barnstable–Yarmouth, MAMSA (162,582 residents), and the Portland, ME MSA (243,537 residents). In order to preserve county boundaries in the New England area, the borders of these MSA's and PMSA's have been expanded to include the non-MSA portions of the counties in which they lie. Thus, this region includes all of Litchfield county, CT: 34,677 residents of the Danbury, CT PMSA and 41,784 residents of the Waterbury, CT PMSA.

The **Albany to Niagra** air quality region (4,435,206 residents) consists of a band of seven MSA's running west from the Pittsfield, MA area to the Niagra Falls, NY area (43,315 km² with 102 residents per km²). These MSA's from east to west include the Pittsfield, MA MSA (84,699 residents plus 50,254 residents of Berkshire county, MA who reside outside the MSA), the Albany–Schenectady–Troy, NY MSA (875,583 residents), the Glens Falls, NY MSA (124,345 residents), the Utica–Rome, NY MSA (299,896), the Syracuse, NY MSA (732,117 residents), the Rochester, NY MSA (1,098,201 residents), and the Buffalo–Niagra Falls, NY MSA (1,170,111 residents).

The **Scranton–Harrisburg** air quality region (3,407,205 residents) consists a band of six MSA's (24,504 km² with 139 residents per km²) that are located just west of the Philadelphia and New York regions. These MSA's include the Scranton–Wilkes-Barre–Hazleton, PA MSA (624,776 residents), the Allentown–Bethlehem–Easton, PA MSA (637,958 residents), the Reading, PA MSA (373,638 residents), the Harrisburg–Lebanon–Carlisle, PA MSA (629,401 residents), the Lancaster, PA MSA (470,658 residents), and the York, PA MSA (381,751 residents). This region also includes Monroe county, PA (138,687 residents); an isolated, non-MSA county just northeast of the Allentown–Bethlehem–Easton, PA MSA.

The **Pittsburgh to Cleveland** air quality region (7,087,165 residents) consists of a contiguous band of eight MSA's/CMSA's from Pittsburgh, PA to Cleveland, OH(36,562 km² with 194 residents per km²). These MSA's include the Pittsburgh, PA MSA (2,358,695 residents), the Sharon, PA MSA (120,293 residents), the Steubenville–Weirton, OH–WV MSA (132,008 residents), the Wheeling, WV–OH MSA (153,172 residents), the Canton–Massillon, OHMSA (406,934 residents), the Erie, PA MSA (280,843 residents), the Youngstown–Warren, OH MSA (594,746 residents), and the Cleveland–Akron, OH CMSA. The Cleveland–Akron, OH CMSA includes the Akron, OH PMSA (694,960 residents) and the Cleveland–Lorain–Elria, OH PMSA (2,250,871 residents).

The **Toledo–Detroit–Flint** air quality region (6,074,631 residents) consists of the Toledo, OH MSA (618,203 residents) and the Detroit–Ann Arbor–Flint, MI CMSA (20,631 km<sup>2</sup> with 294 residents per km<sup>2</sup>). The Detroit–Ann Arbor–Flint, MI CMSA includes the Ann Arbor, MI PMSA (578,736 residents), the Detroit, MI PMSA (4,441,551 residents), and the Flint, MI PMSA (436,141 residents).

The **Milwaukee–Chicago–Gary** air quality region (10,847,112 residents) consists of the Chicago–Gary–Kenosha, IL–IN–WI CMSA and the Milwaukee–Racine, WI CMSA (22,742 km² with 477 residents per km²). The Chicago–Gary–Kenosha, IL–IN–WI CMSA includes the Gary, IN PMSA (631,362 residents), the Chicago, IL PMSA (8,272,768 residents), the Kankakee, IL PMSA (103,833 residents), and the Kenosha, WI PMSA (149,577 residents). The Milwaukee–Racine, WI CMSA includes the Milwaukee–Waukesha, WI PMSA (1,500,741 residents) and the Racine, WI PMSA (188,831 residents).

The **Minneapolis–St. Paul** air qualityregion (2,968,806 residents) consists of the Minneapolis–St. Paul, MN–WI MSA (16,349 km² with 182 residents per km²).

The **Richmond to Norfolk** air quality region (2,566,053 residents) consists two contiguous MSA's in central Virginia (13,845 km² with 185 residents per km²) including the Richmond–Petersburg, VA MSA (996,512 residents) and the Norfolk–Virginia Beach–Newport News, VA–NC MSA (1,569,541 residents).

The **Raleigh to Greenville** air quality region (4,901,184 residents) consists of a band of four contiguous MSA's running from central North Carolina to the western tip of South Carolina along two interstate corridors (36,347 km² with 135 residents per km²). These four MSA's include the Raleigh-Durham-Chapel Hill, NC MSA (1,187,941 residents), the Greensboro-Winston-Salem-High Point, NC MSA (1,251,509 residents), the Charlotte-Gastonia-Rock Hill, NC-SC MSA (1,499,293 residents), and the Greenville-Spartanburg-Anderson, SC MSA (962,441 residents).

The **Atlanta** air quality region (4,112,198 residents) consists of the Atlanta, GA MSA (15,880 km² with 259 residents per km²).

The **Florida Peninsula** air quality region (14,520,138 residents) consists of 40 counties in the Florida peninsula (96,957 km² with 150 residents per km²). This air quality region includes 13 non-MSA counties in the Florida peninsula south of Gainesville, FL and 15 MSA's: Jacksonville, FL (1,100,491 residents); Gainesville, FL(217,955 residents); Dayton Beach, FL (493,175 residents); Ocala, FL (258,916 residents); Orlando, FL (1,644,561 residents); Melbourne–Titusville–Palm Bay, FL (476,230 residents); Lakeland–Winter Haven, FL (483,924 residents); Tampa–St. Petersburg–Clearwater, FL (2,395,997 residents); Sarasota–Bradenton, FL (589,959 residents); Punta Gorda, FL (141,627 Residents); Fort Myers–Cape Coral, FL (440,888 residents); Naples, FL(251,377 residents); Fort Pierce–Port St. Lucie, FL (319,426 residents); West Palm Beach–Boca Raton, FL (1,131,184 residents); and Miami–Fort Lauderdale, FL (3,876,380 residents).

The **Pensacola to New Orleans** air quality region (3,528,105 residents) consists of a band of five contiguous MSA's running along the Gulf coast from Pensacola, FL to New Orleans, LA (34,896 km² with 101 residents per km²). These MSA's include the Pensacola, FL MSA (412,153 residents), the Mobile, AL MSA (540,258 residents), the Biloxi–Gulfport–Pascagoula, MS MSA (363,988 residents), the Baton Rouge, LA MSA (602,894 residents), and the New Orleans, LA MSA (1,337,726 residents).

The **Houston** air quality region (4,669,571 residents) consists of the Houston–Galveston–Brazoria, TX CMSA (20,201 km<sup>2</sup> with 231 residents per km<sup>2</sup>). The Houston–Galveston–Brazoria, TX CMSA includes the Brazoria, TX PMSA (241,767 residents), the Galveston–Texas City, TX PMSA (250,158 residents), and the Houston, TX PMSA (4,177,646 residents).

The **Dallas/Fort Worth** air quality region (5,221,801 residents) consists of the Dallas–Fort Worth, TX CMSA (24,060 km<sup>2</sup> with 217 residents per km<sup>2</sup>). The Dallas–Fort Worth, TX CMSA includes the Dallas, TX PMSA (3,519,176 residents) and the Fort Worth–Arlington, TX PMSA (1,702,625 residents).

The **St. Louis** air quality region (2,603,607 residents) consists of the St. Louis, MO–IL MSA (16,733 km² with 156 residents per km²).

The **Front Range** (**Denver**) air quality region (3,573,008 residents) consists of a band of five contiguous MSA's running just east of the front range of the Rocky Mountains (47,364 km² with 75 residents per km²). These MSA's include the Cheyenne, WY MSA (81,607 residents), the Fort Collins–Loveland, CO MSA (251,494 residents), the Denver–Boulder–Greeley, CO CMSA, the Colorado Springs, CO MSA (516,929 residents), and the Pueblo, CO MSA (141,472 residents). The Denver–Boulder–Greeley, CO CMSA includes the Boulder–Longmont, CO PMSA (291,288 residents), the Denver, CO PMSA (2,109,282 residents), and the Greeley, CO PMSA (180,936 residents).

The **Phoenix–Mesa** air quality region (3,251,876 residents) consists of the Phoenix–Mesa, AZ MSA. The Phoenix–Mesa air quality region includes over 37,212 km<sup>2</sup> (87 residents per km<sup>2</sup>) due to the large size of Arizona counties, but most of the population resides in a denser urban core.

The **Los Angeles/San Diego** air quality region (19,187,478 residents) consists of the San Diego, CA MSA (2,813,833 residents) and the Los Angeles–Riverside–Orange County, CA CMSA (98,535 km² with 195 residents per km²). The Los Angeles–Riverside–Orange County, CA CMSA includes the Los Angeles–Long Beach, CA PMSA (9,519,338 residents), the Orange County, CA PMSA (2,846,289 residents), the Riverside–San Bernardino, CA PMSA (3,254,821 residents), and the Ventura, CA PMSA (753,197 residents). The effective population density of this urban region is understated due to the inclusion of two large counties: San Bernardino and Riverside.

The **San Francisco** air quality region (7,039,362 residents) consists of the San Francisco–Oakland–San Jose, CA CMSA (19,058 km<sup>2</sup> with 369 residents per km<sup>2</sup>). The San Francisco–Oakland–San Jose, CA CMSA includes the Oakland, CA PMSA (2,392,557 residents), the San Francisco, CA PMSA (1,731,183 residents), the San Jose, CA PMSA (1,682,585 residents), the Santa Cruz–Watsonville, CA PMSA (255,602 residents), the Santa Rosa, CA PMSA (458,614 residents), and the Vallejo–Fairfield–Napa, CA PMSA (518,821 residents).

The **Seattle–Tacoma** air quality region (3,554,760 residents) consists of the Seattle–Tacoma–Bremerton, WA CMSA (18,528 km² with 192 residents per km²). The Seattle–Tacoma–Bremerton, WA CMSA includes the Bremerton, WA PMSA (231,969 residents), the Olympia, WA PMSA (207,355 residents), the Seattle–Bellevue–Everett, WA PMSA (3,554,760 residents), and the Tacoma, WA PMSA (700,820 residents).

# **Large City Regions**

The **Portland** air quality region (2,265,223 residents) consists of the Portland–Salem, OR–WA CMSA (18,153 km<sup>2</sup> with 125 residents per km<sup>2</sup>). The Portland–Salem, OR–WA CMSA includes the Portland–Vancouver, OR–WA PMSA (1,918,009 residents) and the Salem, OR PMSA (347,214 residents).

The **Cincinnati** air quality region (1,979,202 residents) consists of the Cincinnati–Hamilton, OH–KY–IN CMSA (9,932 km² with 199 residents per km²). The Cincinnati–Hamilton, OH–KY–IN CMSA consists of the Cincinnati, OH–KY–IN PMSA (1,646,395 residents) and Hamilton–Middletown, OH PMSA (332,807 residents).

The **Sacramento** air quality region (1,796,857 residents) consists of the Sacramento–Yolo, CA MSA (13,488 km² with 133 residents per km²).

The **Kansas City** air quality region (1,776,062 residents) consists of the Kansas City, MO–KS MSA (13,945 km² with 127 residents per km²).

The **Provo–Salt Lake City** air quality region (1,702,450 residents) consists two contiguous MSA's that are located in northern Utah (10,908 km² with 156 residents per km²). These MSA's include the Provo–Orem, UT MSA (368,536 residents) and the Salt Lake City–Ogden, UT MSA (1,333,914 residents).

The **Indianapolis** air quality region (1,607,486 residents) consists of the Indianapolis, IN MSA (9,276 km<sup>2</sup> with 173 residents per km<sup>2</sup>).

The **San Antonio** air quality region (1,592,383 residents) consists of the San Antonio, TX MSA (8,607 km² with 185 residents per km²).

The **Las Vegas** air quality region (1,563,282 residents) consists of the Las Vegas, NV–AZ MSA. The Las Vegas air quality region includes over 101,830 km² (15 residents per km²) due to the large size of Nevada counties, but most of the population resides in a denser urban core.

The **Columbus** air quality region (1,540,157 residents) consists of the Columbus, OH MSA (8,211 km² with 188 residents per km²).

The **Austin–San Marcos** air quality region (1,249,763 residents) consists of the Austin–San Marcos, TX MSA (10,999 km<sup>2</sup> with 114 residents per km<sup>2</sup>).

The **Nashville** air quality region (1,231,311 residents) consists of the Nashville, TN MSA (10,576 km² with 116 residents per km²).

The **Memphis** air quality region (1,135,614 residents) consists of the Memphis, TN–AR–MS MSA (7,855 km<sup>2</sup> with 145 residents per km<sup>2</sup>).

The **Grand Rapids** air quality region (1,088,514 residents) consists of the Grand Rapids–Muskegon–Holland, MI MSA (7,302 km² with 149 residents per km²).

The **Oklahoma City** air quality region (1,083,346 residents) consists of the Oklahoma City, OK MSA (10,998 km² with 99 residents per km²).

The **Louisville** air quality region (1,025,598 residents) consists of the Louisville, KY–IN MSA (5,324 km² with 193 residents per km²).

The **Dayton** air quality region (950,558 residents) consists of the Dayton–Springfield, OH MSA (4,274 km² with 222 residents per km²).

The **Fresno** air quality region (922,516 residents) consists of the Fresno, CA MSA (20,659 km<sup>2</sup> with 45 residents per km<sup>2</sup>).

The **Birmingham** air quality region (921,106 residents) consists of the Birmingham, AL MSA (8,198 km² with 112 residents per km²).

The **Tucson** air quality region (843,746 residents) consists of the Tucson, AZ MSA. The Tucson air quality region includes over 23,627 km<sup>2</sup> (36 residents per km<sup>2</sup>) due to the large size of Arizona counties, but most of the population resides in a denser urban core.

The **Tulsa** air quality region (803,235 residents) consists of the Tulsa, OK MSA (13,203 km<sup>2</sup> with 61 residents per km<sup>2</sup>).

The **El Paso** air quality region (679,622 residents) consists of the El Paso, TX MSA (2,543 km<sup>2</sup> with 267 residents per km<sup>2</sup>).

# Rural Regions

The **Northern New England** air quality region (2,241,468 residents) consists of 42 counties (149,718 km² with 15 residents per km²) north of the Boston/Providence/Hartford and Albany to Niagra air quality regions. This rural air quality region includes the Bangor, ME MSA (90,864 residents), the Lewiston–Auburn, ME MSA (90,830 residents), and the Burlington, VT MSA (169,391 residents).

The **Northern Appalachia** air quality region (3,588,349 residents) consists of 55 counties (107,402 km² with 33 residents per km²) of the Appalachian Region in New York and Pennsylvania north of the Mason-Dixon line (aside from one rural county in southwestern Pennsylvania). This rural air quality region includes the Jamestown, NY MSA (139,750 residents), the Elmira, NY MSA (91,070 residents), the Binghamton, NY MSA (252,320 residents), the Williamsport, PAMSA (120,044 residents), the State College, PA MSA (135,758 residents), the Johnstown, PA MSA (232,621 residents), and the Altoona, PA MSA (129,144 residents).

The **Central Appalachia** air quality region (2,537,893 residents) consists of 87 counties (98,645 km<sup>2</sup> with 26 residents per km<sup>2</sup>) of the Appalachian Region in Ohio and in Maryland, West Virginia and Virginia south of the Mason-Dixon line (aside from one rural county in southwestern Pennsylvania). This rural air quality region includes the Cumberland, MD–WV MSA (102,008 residents) and the Charleston, WV MSA (251,662 residents).

The **South Central Appalachia** air quality region (1,566,683 residents) consists of 71 counties (65,669 km<sup>2</sup> with 24 residents per km<sup>2</sup>) of the Appalachian Region in eastern Kentucky and Tennessee. This rural air quality region contains no MSA's.

The **Southeastern Appalachia** air quality region (2,154,049 residents) consists of 54 counties (53,304 km² with 40 residents per km²) of the Appalachian Region in western North Carolina and northern Georgia. This rural air quality region includes the Hickory–Morganton–Lenoir, NC MSA (341,851 residents), the Asheville, NC MSA (225,965 residents), and the Athens, GA MSA (153,444 residents).

The **Bluegrass** air quality region (1,410,263 residents) consists of 41 counties (37,115 km<sup>2</sup> with 38 residents per km<sup>2</sup>) in western Kentucky and Tennessee. This rural air quality region includes the Lexington, KY MSA (479,198 residents) and the Clarksville–Hopkinsville, TN–KY MSA (207,033 residents).

The **Piedmont** air quality region (2,093,921 residents) consists of 61 counties (59,493 km<sup>2</sup> with 35 residents per km<sup>2</sup>) central Virginia and eastern North Carolina. This rural air quality region includes five MSA's: Charlottesville, VA (159,576 residents); Roanoke, VA (235,932 residents); Lynchburg, VA (214,911 residents); Danville, VA (110,156 residents), and Rocky Mount, NC (143,026 residents).

The **Southeast** air quality region (6,697,074 residents) consists of 171 counties (203,124 km² with 33 residents per km²) from central North Carolina to eastern Alabama. This rural air quality region includes 13 MSA's: Goldsboro, NC (113,329 residents); Fayetteville, NC (302,963 residents); Florence, SC (125,761 residents); Columbia, SC (536,691 residents); Sumter, SC (104,646 residents); Augusta–Aiken, GA–SC (477,441 residents); Athens, GA (153,444 residents); Macon, GA (322,549 residents); Albany, GA (120,822 residents); Columbus, GA–AL (274,624 residents); Auburn–Opelika, AL (115,092 residents); and Dothan, AL (137,916 residents).

The **South Central** air quality region (4,419,205 residents) consists of 127 counties (205,746 km<sup>2</sup> with 22 residents per km<sup>2</sup>) in western Alabama and Tennessee and eastern Mississippi. This rural air quality region includes 6 MSA's: Gadsden, AL (103,459 residents); Anniston, AL (112,249 residents); Montgomery, AL (333,055 residents); Tuscaloosa, AL (164,875 residents); Jackson, MS (440,801 residents); Hattiesburg, MS (111,674 residents); and Jackson, TN (107,377 residents).

The **West South Central** air quality region (2,723,327 residents) consists of 71 counties (141,131 km² with 19 residents per km²) in northwestern Louisiana, eastern Texas and southwest Arkansas. This rural air quality region includes six MSA's: Alexandria, LA (126,337 residents); Monroe, LA (147,250 residents); Shreveport–Bossier City, LA (392,302 residents); Texarkana, TX–Texarkana, AR (129,749 residents); Longview–Marshall, TX (208,780 residents); and Tyler, TX (174,706 residents).

The **Eastern Mid-West** air quality region (6,486,226 residents) consists of 114 counties (128,926 km² with 50 residents per km²) in western Ohio, Indiana, and southern Michigan. This semi-rural air quality region includes 15 MSA's: Mansfield, OH (175,818 residents); Lima, OH (155,084 residents); Jackson, MI (158,422 residents); Lansing–East Lansing, MI (447,728 residents); Kalamazoo–Battle Creek, MI (452,851 residents); Benton Harbor, MI (162,453 residents); South Bend, IN (265,559 residents); Fort Wayne, IN (502,141 residents); Elkhart–Goshen, IN (182,791 residents); Muncie, IN (118,769 residents); Kokomo, IN (101,541 residents); Lafayette, IN (182,821 residents); Terre Haute, IN (149,192 residents); and Bloomington, IN (120,563 residents).

The **Central Mid-West** air quality region (11,927,428 residents) consists of 363 counties (569,631 km<sup>2</sup> with 21 residents per km<sup>2</sup>) in Illinois, southern Wisconsin, Iowa, Missouri, northern

Arkansas, and eastern Kansas and Nebraska. This rural air quality region includes 22 MSA's: Champaign—Urbana, IL (179,669 residents); Decatur, IL (114,706 residents): Bloomington—Normal, IL (150,433 residents); Peoria—Perkin, IL (347,387 residents); Springfield, IL (201,437 residents); Davenport—Moline—Rock Island, IA—IL (359,062 residents); Rockford, IL (371,236 residents); Janesville—Beloit, WI (152,307 residents); Madison, WI (426,526 residents); Dubuque, IA (89,143 residents); Cedar Rapids, IA (191,701 residents); Iowa City, IA (111,006 residents); Waterloo—Cedar Falls, IA (128,012 residents); Des Moines, IA (456,022 residents); Sioux City, IA—NE (124,130 residents); Omaha, NE—IA (716,998 residents) Lincoln, NE (250,291 residents); St. Joseph, MO (102,490 residents); Columbia, MO (135,454 residents); Wichita, KS (545,220 residents); Topeka, KS (169,871 residents); Lawrence, KS (99,962 residents); and Jonesboro, AR (82,148 residents).

The **North Michigan** air quality region (1,458,632 residents) consists of 39 counties (58,549 km<sup>2</sup> with 25 residents per km<sup>2</sup>) in Michigan north of a line between Grand Rapids and Flint. This rural air quality region includes the Saginaw–Bay City–Midland, MI MSA (403,070 residents).

The **Upper Mid-West** air quality region (5,549,381 residents) consists of 178 counties (422,834 km<sup>2</sup> with 13 residents per km<sup>2</sup>) in the Michigan peninsula, northern Wisconsin and Iowa, Minnesota, and the eastern edges of North and South Dakota along the Red River. This rural air quality region includes 12 MSA's: Sheboygan, WI (112,646 residents); Green Bay, WI (226,778 residents); Appleton–Oshkosh–Neenah, WI (358,365 residents); Wausau, WI (125,834 residents); Eau Claire, WI (148,337 residents); La Crosse, WI (126,838 residents); Rochester, MN (124,277 residents); St. Cloud, MN (167,392 residents); Duluth–Superior, MN–WI (243,815 residents); Grand Forks, ND–MN (97,478 residents); Fargo–Moorhead, ND–MN (174,367 residents) and Sioux Falls, SD (172,412 residents).

The **Central Texas / Oklahoma** air quality region (2,212,566 residents) consists of 71 counties (151,668 km² with 15 residents per km²) in central Oklahoma and Texas. This rural air quality region includes five MSA's: Enid, OK (57,813 residents); Waco, TX (213,517 residents); Killeen–Temple, TX 312,952 residents); Sherman–Denison, TX (110,595 residents); and Bryan–College Station, TX (152,415 residents).

The **Ozark Plateau** air quality region (2,404,760 residents) consists of 65 counties (124,454 km<sup>2</sup> with 19 residents per km<sup>2</sup>) in northwestern Arkansas, eastern Oklahoma, and southwestern Missouri. This rural air quality region includes 4 MSA's: Fort Smith, AR–OK (207,290 residents); Fayetteville–Springdale–Rogers, AR (311,121 residents); Joplin, MO (157,322 residents); and Springfield, MO (325,721 residents).

The California Central Valley air quality region (3,226,466 residents) consists of 24 counties (96,804 km² with 33 residents per km²) in the central valley of California. This rural air quality region includes six MSA's: Bakersfield, CA (661,645 residents); Visalia–Tulare–Porterville, CA (368,021 residents); Merced, CA (210,554 residents); Modesto, CA (446,997 residents); Stockton–Lodi, CA (563,598 residents); Yuba City, CA (139,149 residents); Chico–Paradise, CA (203,171 residents); and Redding, CA (163,256 residents).

The **Columbia Plateau** air quality region (1,060,554 residents) consists of 17 counties (61,251 km<sup>2</sup> with 17 residents per km<sup>2</sup>) in western Washington. This rural air quality region includes the Spokane, WA MSA (417,939 residents) and the Richland–Kennewick–Pasco, WA MSA (191,822 residents).

# Valley Regions

The **Ohio Valley** air quality region (1,500,130 residents) consists of the 45 counties (41,769 km<sup>2</sup> with 36 residents per km<sup>2</sup>) along the Ohio River Valley from the Steubenville, OH MSA to the Mississippi River. This region includes the Parkersburg–Marietta, WV–OH MSA (151,237 residents), the Huntington–Ashland, WV–KY–OH MSA (315,538 residents), the Evansville–Henderson, IN–KY MSA (296,195 residents) and the Owensboro, KY MSA (91,545 residents), but does not include the Cincinnati, OH, MSA or the Louisville, KY–IN MSA.

The **Upper Tennessee Valley** air quality region (1,846,978 residents) consists of 25 counties (23,363 km<sup>2</sup> with 79 residents per km<sup>2</sup>) in eastern Tennessee and southwestern Virginia along the Tennessee River. This region includes the Johnson City–Kingsport–Bristol, TN–VA MSA (480,091 residents), the Knoxville, TN MSA (687,249 residents), and the Chattanooga, TN–GA MSA (465,161 residents).

The **Lower Tennessee Valley** air quality region (1,002,471 residents) consists of 21 counties (29,193 km² with 34 residents per km²) in Alabama and western Tennessee along the Tennessee River. This region includes the Huntsville, AL MSA (342,376 residents), the Decatur, AL MSA (145,867 residents), and the Florence, AL MSA (142,950 residents).

The **Lower Mississippi Valley** air quality region (1,733,195 residents) consists of 54 counties (78,284 km<sup>2</sup> with 22 residents per km<sup>2</sup>) from southern Illinois and Missouri to the Gulf of Mexico along the Mississippi River and a portion of the lower Red River in Arkansas. This region includes the Little

Rock-North Little Rock, AR MSA (583,845 residents) and the Pine Bluff, AR MSA (84,278 residents), but does not include the Memphis, TN-AR-MS MSA or the Lafayette, LA MSA.

# Coastal Regions

The **Mid-Atlantic Coast** air quality region (801,504 residents) consists of 21 counties (18,776 km<sup>2</sup> with 43 residents per km<sup>2</sup>) in eastern Virginia and on the DelMarVa peninsula that are bounded by the Richmond–Petersburg, VA MSA, the Washington–Baltimore, DC–MD–VA–WV CMSA, and the Philadelphia–Wilmington–Atlantic City, PA–NJ–DE–MD CMSA. This region includes the Dover, DE MSA (126,697 residents).

The **Southeast Coast** air quality region (2,770,723 residents) consists of 48 counties (71,641 km<sup>2</sup> with 39 residents per km<sup>2</sup>) along the Atlantic coast from North Carolina to Georgia. This region includes the Greenville, NC MSA (133,798 residents), the Jacksonville, NC MSA (150,355 residents), the Wilmington, NC MSA (233,450 residents), the Myrtle Beach, SC MSA (196,629 residents), the Charleston–North Charleston, SC MSA (549,033 residents), and the Savannah, GA MSA (293,000 residents).

The **East Gulf Coast** air quality region (713,116 residents) consists of 18 counties (31,225 km<sup>2</sup> with 23 residents per km<sup>2</sup>) along the Gulf coast in the Florida panhandle. This region includes the Tallahassee, FL MSA (284,539 residents), the Panama City, FL MSA (148,217 residents), and the Fort Walton Beach, FL MSA (170,498 residents).

The **Central Gulf Coast** air quality region (1,481,780 residents) consists of 19 counties (40,488 km² with 37 residents per km²) along the Gulf coast from the New Orleans to the Houston. This region includes the Houma, LA MSA (194,477 residents), the Lafayette, LA MSA (385,647 residents), the Lake Charles, LA MSA (183,577 residents), and the Beaumont–Port Arthur, TX MSA (385,090 residents), but does not include the Houston–Galveston–Brazoria, TX MSA or the New Orleans, LA MSA.

The **Western Gulf Coast** air quality region (996,651 residents) consists of 13 counties (28,138 km² with 35 residents per km²) along the Gulf coast of Texas from Houston to the Mexican border. This region includes the Victoria, TX MSA (84,088 residents), the Corpus Christi, TX MSA (380,783 residents), and the Brownsville–Harlingen–San Benito, TX MSA (335,227 residents).

The **California Coast** air quality region (1,101,024 residents) consists of 4 counties (27,653 km<sup>2</sup> with 40 residents per km<sup>2</sup>) along the Pacific coast of southern California. This region includes the Salinas, CA MSA (401,762 residents), the San Luis Obispo–Atascadero–Paso Robles, CA MSA (246,681 residents), and the Santa Barbara–Santa Maria–Lompoc, CA MSA (399,347 residents).

The **North Pacific Coast** air quality region (2,056,047 residents) consists of 28 counties (128,492 km² with 16 residents per km²) along the Pacific coast from the Canadian border to northern California. This region includes the Bellingham, WA MSA (166,814 residents), the Corvallis, OR MSA (78,153 residents), the Medford–Ashland, OR MSA (181,269 residents), and the Eugene–Springfield, OR MSA (322,959 residents).

## Extremely Low-density Regions

The **High Plains** air quality region (2,021,475 residents) consists of 223 counties (858,648 km<sup>2</sup> with 2.4 residents per km<sup>2</sup>) east of the Rocky Mountains from southern Colorado to the Canadian Border. This region includes the Billings, MT MSA (129,352 residents), the Casper, WY MSA (66,533 residents), the Rapid City, SD MSA (88,565 residents), and the Bismark, ND MSA (94,719 residents).

The **Great Plains** air quality region (2,070,401 residents) consists of 126 counties (381,355 km<sup>2</sup> with 5.4 residents per km<sup>2</sup>) in northern Texas, eastern Oklahoma, southwest Kansas, southeastern Colorado, and northeasternNew Mexico. This region includes the Abilene, TX MSA (126,555 residents), the Amarillo, TX MSA (217,858 residents), the Lubbock, TX MSA (242,628 residents), the Wichita Falls, TX MSA (140,518 residents), and the Lawton, OK MSA (114,996 residents).

The **Southwest** air quality region (4,478,318 residents) consists of 97 counties (687,524 km² with 6.5 residents per km²) from southern Texas, through New Mexico and Arizona, to southern California. This region includes eight MSA's: McAllen–Edinburg–Mission, TX (569,463 residents); Laredo, TX (193,117 residents); San Angelo, TX (104,010 residents); Odessa–Midland, TX (237,132 residents); Las Cruces, NM (174,682 residents); Sante Fe, NM (147,635 residents); Albuquerque, NM (712,738 residents); and Yuma, AZ (160,026 residents).

The **Rocky Mountains** air qualityregion(2,206,886 residents) consists of 118 counties (717,574 km<sup>2</sup> with 3.1 residents per km<sup>2</sup>) along the Rocky Mountains from southern Colorado to the Canadian Border. This region includes the Grand Junction, CO MSA (116,255 residents), the Pocatello, ID MSA (75,565 residents), the Missoula, MT MSA (95,802 residents), and the Great Falls, MT MSA (80,357 residents).

The **Great Basin** air quality region (1,235,556 residents) consists of 43 counties (457,727 km<sup>2</sup> with 2.7 residents per km<sup>2</sup>) from northern Arizona through eastern Nevada and western Utah into southwestern Idaho and western Oregon. This region includes the Flagstaff, AZ–UT MSA (122,366 residents) and the Boise City, ID MSA (432,345 residents).

The **Coastal Range** air quality region (1,280,350 residents) consists of the 31 counties (257,711 km<sup>2</sup> with 5.0 residents per km<sup>2</sup>) from California to Washington along the Sierra Nevada, Coastal and Cascade mountain ranges. This region includes the Reno, NV MSA (339,486 residents) and the Yakima, WA MSA (222,581 residents).

## Section 5. Ambient Air Quality Monitoring Quality System Strategy

#### 5.1 Introduction

Since the implementation of the ambient air monitoring program, there has been little change to the quality assurance (QA) regulations and the resultant quality system for the program. As new monitoring programs were developed (e.g.,  $PM_{2.5}$ ), new regulations were added. But little thought was given to a review of the overall system for ensuring the quality of the nations data.

Within the same period of time, changes within monitoring and QA have taken place:

- The National Performance Audit Program saw a reduction in funding which resulted in fewer audits being distributed.
- Monitoring technology has changed making instruments more reliable and stable.
- New QA processes, like data quality objectives, performance based measurement systems, and data quality assessments, have been developed.
- EPA QA policy has been revised in areas like the development of quality management plans and quality assurance project plans.

With the re-thinking of the monitoring process should also come a re-thinking of the processes of ensuring the quality of our data. This section will address a strategy for the review and if necessary redevelopment of a quality system that is germane, flexible where necessary, and responsive to changes in the monitoring program.

## **5.1.1.** The Quality System

An important concern in any organization that is collecting and evaluating environmental data must be the quality of the results. A quality system must be developed and documented to ensure that the monitoring results:

- meet a well-defined need, use, or purpose;
- satisfy customers expectations;
- comply with applicable standards and specifications;
- comply with statutory (and other) requirements; and
- reflect consideration of cost and economics.

A quality system is defined as a structured and documented management system describing the policies, objectives, principles, organizational authority, responsibilities, and implementation plan of an organization for ensuring quality in its work processes, products, and services. The quality system provides the framework for planning, implementing, assessing, and reporting worked performed by the organization and for carrying out required QA and quality control (QC).

The development of a quality system requires a coordinated effort between stakeholders: EPA Headquarters, the EPA Regions, and the SLT monitoring community. As the strategy is presented, roles and responsibilities of the stakeholders will be identified and discussed.

# **5.2** Quality System Review/Improvement Process

The goal for this QA Strategy is to take a philosophical look at QA with the premise: "what are appropriate quality system elements and activities for an ambient air monitoring program"? Once this is determined, any monitoring program would address the quality system elements/activities in an appropriate manner for their objectives, thereby creating some flexibility in the approach to data quality (i.e., a graded approach to QA).

In maintaining consistency with the Strategy objectives, it was felt that the best way to improve the Ambient Air Monitoring Program quality system was to thoroughly review the current program in light of new quality assurance concepts and policy. This review had supporting goals to:

- develop an understanding and respect of the various stakeholder goals for collecting ambient air monitoring data and the various levels of acceptable data quality;
- provide a structure in which the elements vital to a healthy QA program are intimately tied to the monitoring program (i.e., are funded commensurate with ambient air monitoring);
- provide an integrated (SLT/Region/Headquarters) approach to ambient air quality monitoring quality system development and implementation;
- review and solidify roles and responsibilities;
- move towards the development of performance based measurements and assessments to identify acceptable data quality;
- eliminate redundancies to improve cost efficiencies;
- establish a graded quality system approach to allow resource prioritization toward measurement systems that are classified as critical;
- provide a thorough review of regulations in order to identify requirements and those elements that could be considered guidance;
- revise regulations (CFR) and guidance (Red Book, Vol. II) to reflect the new recommendations;
- create an atmosphere of stakeholder cooperation and commitment toward implementing the quality system; and
- establish a phased approach toward implementation, with a flexible timeline to assure that each step is thoroughly completed.

In order to accomplish these goals a QA Strategy Workgroup (Workgroup) was developed. The Workgroup is composed of staff members from EPA Headquarters, EPA

Regions, and SLTs. To meet the established goals, the Workgroup developed some fundamental characteristics for QA changes. The QA system should be:

- performance based;
- workable;
- based on common sense;
- based on good science;
- flexible;
- defendable and comparable;
- balanced against legal requirements;
- covering both spectrums of air program expertise; and
- implementable

The Workgroup created a list separating the current QA activities into the three elements: 1) planning, 2) implementation, and 3) assessment/reporting. (See **Table 5-1.**) In order to address each QA activity in a consistent manner, an Ambient Air Monitoring Quality System Activity Information Form was developed, as shown in **Figure 5-1.** This process has provided a record of the evaluation of each QA activity, and has further provided the direction to recommend the changes in both regulation and guidance documentation.

Table 1 OA Element and Activity List

Quality System Elements	Activities and Questions
Planning	Activities  Data Quality Objectives Regulation Development Quality Management Plans QA Project Plans and SOPs Guidance Documents -Network Design -Methods -QA Manuals
Implementation	Activities  < Training  < Internal Quality Control Activities  -precision checks (automated/manual)  -verification/calibration (zero/span checks, flow rate checks etc)  - QC described in CFR and guidance ( MQO tables in Redbook APP 3)  -standards certification  -instrument and equipment maintenance  < Record keeping  < Data verification/validation
Assessment/ Reporting	Activities  < Site Characterizations < Performance Evaluations (NPAP, PEP, Region/SLT Performance audits) < Management Systems Reviews < Technical Systems Audits < Data Quality Assessments < QA Reports < P&A Reports

Ambient Air Monitoring Quality System Activity Information Form			
Quality System Element:(Planning, Implementation, Assessment/Reporting)  Quality System Activity:			
Activity Description:  Definition Actions covered under this description What is the function or use of this activity? Is the activity important? (what does it get us) Is there a product? Who is the major user of the product or information Is this a new activity? What activity does it replace or enhance? Brief description of current activities Who is responsible for the activity (currently)			
Pros and Cons of the activity as it's currently implemented:  Ways of improving the activity:  Who should be providing (responsible for) this activity?  Are changes to regulation or guidance required?			

Figure 5.1. Ambient Air Monitoring Quality System Activity Information Form

The Workgroup process is expected to be completed over a period of several years, likely concluding by 2004. Over 80 QA action items were identified (see **Attachment 5.1**) and prioritized. As recommendations are completed by the Workgroup, they will be provided to the NMSC for review. The NMSC will evaluate these for content and consistency with the overall Strategy objectives. A summary of Workgroup activities to-date are provided in **Attachment 5.2.** The recommendations, which follow in the next subsection, are based primarily on the efforts to-date of the Workgroup.

## **5.3** Recommended Changes

## **5.3.1.** Performance-Based Measurement Process (PBMS)

A performance-based measurement process should be the primary tool for selection or identification of appropriate methods for ambient air monitoring. PBMS is a set of processes wherein the data quality needs, mandates or limitations of a program or

project are specified and serve as criteria for selecting appropriate methods to meet those needs in a cost-effective manner. PBMS can be achieved by using the data quality objective (DQO) process early in the planning process. DQOs need to be developed in concert with the setting of the attainment standards, since population and measurement uncertainty may dictate where the NAAQS is set and what errors can be tolerated. DQOs would then set the stage for the development of federal reference method acceptance criteria that would be in step with the DQO. As an example, the DQOs developed for PM2.5 are now being used to determine the "acceptability" of continuous PM2.5 monitors.

OAQPS would be responsible for developing DQOs for federally mandated data collection efforts. DQOs for other data collection activities (i.e., DQOs for non-trends speciation sites) would be the responsibilities of the SLTs. Relative to NCore, since the monitoring for comparison to the NAAQS would be included in NCore, therefore, DQOs would be developed by OAQPS for monitoring to fulfill this objective.

The performance-based approach that lends itself to flexibility will put more responsibility on the SLTs for developing quality systems. Therefore, there will be a greater importance and emphasis on QA project plans. Recommendations for this category include:

- 1) Completing DQOs for other criteria pollutants Prioritize this activity to ozone and toxics (if necessary). With a coarse particulate matter standard expected, get ahead of the curve for this DQO. As time allows, utilize the DQO process to establish DQOs for the other criteria pollutants.
- 2) Linking DQOs more directly to Federal Reference Method and Equivalency Program It is important to continue implementation of the Federal Reference Method and Equivalency Program, but the acceptance criteria should be linked to the DQOs.
- 3) Using a graded approach to QA Under the Strategy, the use of air monitoring data will have multiple applications. Therefore, some monitoring objectives may not call for quality systems and quality assurance documentation (QAPPS) to meet the stringent requirements for NAAQS comparison purposes.
- **4) Not deploying new network monitors until full testing** A greater level of real-world (e.g., not just laboratory) testing of monitoring equipment needs to occur prior to implementation of new monitoring programs. This will help identify monitor problems and will supply information on population and measurement uncertainties. NCore Level 1 sites (at least one) might be used for testing purposes.
  - 5) Providing more ambient air specific training on the DOO process.
- **6) Providing a vehicle for statistical support on DQOs** OAQPS would establish a contract vehicle that would allow SLTs to tap into statistical help as it relates to DQOs.

## **5.3.2** Roles and Responsibilities

For each aspect of the QA process, there needs to be a clear understanding of the roles and responsibilities for each participant (i.e., OAQPS, EPA Regions, and SLTs). In addition, within the SLT organizations, there should be a responsible QA manager, and to the degree it can be accommodated, a group of people who understand the QA system and are further empowered to implement it. The specific definition of the roles and responsibilities is still a work-in-progress.

## **5.3.3.** Funding/Resource Issues

QA activities need to be intimately tied to the monitoring process so that costs for the quality system increase/decrease commensurately with monitoring costs. Resource and funding related action items include:

- 1) Providing a reasonable estimate of the "cost of QA" Identify quality system elements for a "typical" SLT monitoring organization and provide an estimate of the costs of an adequate quality system. Use these estimates to provide a percentage of monitoring costs that should be allocated to the implementation of a quality system.
- 2) Ensuring funds are available for QA training EPA provides regular and continuing training on many aspects of air programs. It is important to include QA training as part of the overall training program.
- 3) **Providing Contractual Support** There should be a mechanism for OAQPS to allow SLTs to tap into statistical expertise for development of data quality objectives, data quality assessments, and other statistically-related assessments.
- 4) Applying State and Territorial Air Grants (STAG) Resources for NPAP STAG resources should be used to cover the NPAP program. STAG funds currently pay for the PM<sub>2.5</sub> Performance Evaluation Program (PEP). The NPAP program is currently being re-invented to a through-the-probe audit process. The added costs to each state to implement this new program is estimate to be about \$11,000 per year. More information on this suggestion is included in the performance evaluation subsection.

# **5.3.4.** Regulation Changes

Regulations for the Ambient Air Monitoring Program quality system can be found primarily in 40 CFR part 58, Appendix A and Appendix B. However, quality control criteria can also be found in 40 CFR part 50 that describe the method requirements. Efforts to date have focused primarily on part 58. Therefore, this section

will not contain specific regulation changes to a particular pollutant, but will provide recommendations at a broader scale. Recommendations and action items include:

- 1) Reducing confusion between requirements and guidance- In general anything in regulation identified as a "must," "shall" or "will" is considered mandatory. Guidance documents usually supplement the regulation by providing additional information. Guidance documents may provide additional "suggested" methods, quality control samples, or acceptance criteria that are not found in CFR and are, therefore, not mandatory. However there have been cases where CFR requires that guidance documents be followed. This has added some confusion to the traditional use of regulations and guidance documentation.
- 2) Defining a graded approach in CFR- EPA has endorsed using a graded approach for QA, meaning tailoring your quality system and QA project plan development to the objectives for which the data are being collected. For example, developing a quality system for data that will be used to make regulatory decisions would need a "more stringent" quality system than an air monitoring program for environmental education purposes. It is necessary, then, to define and utilize the graded approach as it relates to the collection of ambient air data for different monitoring objectives. The approach needs to provide balance between monitoring objectives and data comparability among programs with similar objectives.
- 3) Combining Part 58 Appendix A and B- Since most of the requirements for Appendix A (SLAMS) and Appendix B (PSD) are the same, the combining of these appendices will be explored.
- 4) Reviewing the requirements, focusing on the "musts" If the performance-based measurement systems are to work, performance goals (DQOs) are needed, and quality control (QC) samples could be used to evaluate the achievement of the goals. However, the frequency of implementing the requirements and some of the actual acceptance criteria may not be required in CFR. These specifics would be included in guidance documents. Therefore, organizations with sophisticated QA programs could have the flexibility to develop their quality systems with minimal hindrance in requirements, while organizations that had less sophisticated programs or expertise could use the guidance to develop their quality systems. Allowing this type of flexibility will put much more emphasis on the development, approval, and use of QA project plan documentation and oversight activities.
- 5) Revising CFR to provide for quarterly data certifications Due to the emphasis on real-time reporting, data quality validation and evaluation is occurring earlier in the monitoring process than in the past. In addition, the QA Reports distributed by OAQPS (i.e., CY99 and CY00 PM2.5 QA Reports) have limited usefulness because the data are not evaluated until after it is officially certified, typically 6 months after the calendar year in which it was collected.

Certifications could occur sooner and a proposal for quarterly certifications is being considered.

## **5.3.5** Training and Guidance

Recommendations and actions items related to training and guidance are as follows:

- 1) Place more emphasis on training- In general, QA training has been neglected, as compared to other air program training activities. Mechanisms for achieving QA training be included in the overall training process for SLTs. Further, by identifying specific training in QAPPs, or as part of technical systems audits recommendations, the training needs are more clearly defined and delineated.
- 2) **Develop "certification/accreditation" programs** One way to place more emphasis on training was to establish a national accreditation process to certify personnel in the following categories:
  - Upper Management (basic QA concepts)
  - Ambient Air Monitoring Manager
  - Site Operator
  - Calibrators
  - QA Technician
  - Laboratory Scientist
  - QA Manager
  - Information Manager

This accreditation process would foster a level of consistency across the nation. SLT organizations need to be creative in how they use and benefit from the accreditation process.

- 3) Conduct a poll for guidance- It is suggested that a poll of SLTs be conducted to determine the total universe of guidance of value. It was suggested that STAPPA/ALAPCO could help develop/implement this poll.
- 4) Combine all guidance into one document Currently, QA guidance is scattered among several documents. There should be one document that could combine all the guidance necessary for ambient air monitoring and associated quality assurance. It is suggested that the QA Handbook Volume II (Redbook) be the home for the various guidance.
- 5) Conduct an annual QA Conference It is recommended that a QA meeting be held annually, similar to the AIRS training. Such a meeting could coincide with the National QA Conference in order to take advantage of the training modules put on by EPA Quality Staff at the National Meeting.

- **6) Develop web-based training programs** OAQPS should pursue the use of web-based training courses.
- 7) **Develop a generic QAPP** Take the G-5 EPA QAPP guidance and develop a generic ambient air monitoring QAPP software product that would allow the SLTs to input the correct information into each section for their particular monitoring program.

## 5.3.6. Data Certification and Quicker Data Access on AIRS

Due to the more recent emphasis on real-time reporting of data, the real-time review/verification/validation of data has become equally important. Because of more timely data assimilation, the current process of certifying a calendar year's worth of data six months after the end of the previous calendar year can be improved. A majority of data verification/validation efforts have already been automated in many state and local agencies. Delays in getting data into AIRS in many cases is simply because the regulations allow it. The QA Report would have more value if it was reported sooner, and accordingly would require earlier certification of data. A number of recommendations on this topic include:

- 1) Providing more automated requirements for data review/verification/validation It is recommended that an initial capital expenditure of information capture and transfer technologies (e.g., data loggers, telemetry, automated quality control) for automatic transfer of routine and quality control information to central facilities be considered. Included in this would be quality control systems for automating various QC checks, like zero/span checks, or bi-weekly precision checks.
- 2) Providing for quarterly certifications- Instead of waiting six months from the end of the calendar year, provide a mechanism for certification on a quarterly basis.
- 3) Certified/uncertified data flagging Data qualifiers are not used for the majority of the criteria pollutants, meaning that SLT personnel wait for data to be validated before uploading to AIRS. Since many SLTs use data qualifiers on their local sites to inform data users that the real time data is not validated, AIRS data could be initially uploaded as "unqualified" and on a quarterly basis, then after validation, have this qualifier removed. This would allow OAQPS to develop generic data evaluation/validation reports on AIRS that could be used or modified by the AIRS user community, rather than having SLTs develop their own reports.
- **4) Developing QA/QC evaluation reports** Opportunities exist to reduce the burden on data validation personnel through the development and generation of various validation/evaluation program reports.

## **5.3.7** Quality Management Plans (QMPs) and QA Project Plans (QAPPs)

Two of the major QA documentation requirements for EPA-funded programs are quality management plans (QMPs) and project specific QA project plans (QAPPs). EPA provides some flexibility on how these documents are prepared. For example, small local agencies may be able to combine their QMP and QAPP into one document. However, there are also some discrepancies among the EPA Regions on the detail and approval process of QMPs and QAPPs. Since the objectives for the current SLAMS monitoring is similar in all parts of the country, there should be some consistency in the preparation/review/approval requirements for QMPs and QAPPs for the ambient air monitoring program.

As mentioned earlier, if the performance-based measurement process is to be successful, the responsibility of creating an adequate quality system will be the responsibility of the SLTs, and not mandated in CFR. The QAPP document, under this quality system, will become more important SLTs, since it will indicate how the organization plans on meeting, with the use of various quality control measures, the performance goals. The Strategy will attempt to foster this paradigm shift.

## **5.3.8.** Quality Control Activities

The majority of the day-to-day QA activities at the SLT monitoring organizations involve implementing or assessing quality control information, whether it be zero/span checks, collocated precision, or running field trip or lab blanks. Each method contains a list of required and suggested quality control samples to judge data acceptability of a phase (sampling) of the measurement system or the total measurement system.

Accordingly, it is recommended that the performance-based measurement system principal be used to develop the necessary quality control samples in the regulations without mandating frequency and acceptance criteria. The CFR should identify the types of QC samples that will provide assessments of attaining the DQOs. As can be shown with the PM2.5 DQO software tool, various combinations of uncertainty (i.e., precision, bias etc.) affect the attainment of the data quality objectives. The CFR would be revised to identify the uncertainties that needed to be measured as well as the confidence one wanted in the estimate of those uncertainties. The SLTs would then be responsible for developing a quality system that would measure, assess, and control these uncertainties. Therefore, the SLTs would determine how frequently they needed to perform various QC checks and what the appropriate acceptance criteria should be. OAQPS, using the data in AIRS, could also assess data uncertainty to determine if an SLT had developed a quality system that was "in control". For organizations with less QA resources or experience, guidance documents would continue to be developed that would provide the suggested acceptance criteria and QC sample frequencies.

### **5.3.9** Site Characterizations

Site characterizations are a type of audit to ensure that samplers or monitors at the monitoring site meet the applicable siting criteria for existing SLAMS, NAMS and PAMS sites, which are now specified in 40 CFR Part 58 Appendix E. The on-site visit consists of the physical measurements and observations such as:

- height above ground level
- proper spacing from various instruments, or
- distance from obstructions and roads.

Recommendations and action items for site characterization that would apply to NCore include:

- 1) Setting minimal levels and tracking The requirements for the frequency of such characterization would be changed, if necessary. In addition, better tracking of this information would ensure adequate site characterizations are being performed. AIRS has an area that can be used for this tracking activity.
- 2) Ensuring updates made in AIRS Information from inspections of monitors or sampling equipment added to site, latitude/longitude changes reflect a needed change in the site record in AIRS. This is not always being done. There needs to be some method of ensuring that information found during the site characterization process gets corrected in AIRS in a timely manner.
- 3) Developing and using a site characterization form. A site characterization form and possibly software could be developed and distributed to provide some consistency in performing site characterizations.
- **4) Site characterization training-** A training module could be developed for the performance of site characterizations.
- 5) Speeding up approvals for discontinued sites- SLTs submit paperwork for discontinuing sites, but EPA approvals often take a considerable length of time. OAQPS needs to review this process and make it more timely.

#### **5.3.10** Performance Evaluations

Performance evaluations (PE) are a type of audit in which the quantitative data generated in a measurement system are obtained independently and compared with routinely obtained data to evaluate the proficiency of an analyst or laboratory. The types of audits in this category include, for example, the National Performance Audit Program (NPAP), Standard Reference Photometer Program (SRP), PM2.5 Performance Evaluation Program (PEP), as well as any SLT's audit programs. Recommendations for improvement include:

- 1) Avoiding redundant programs It is known that the goals of the NPAP program are similar to the goals of various SLT programs (e.g., the California Air Resources Board's through-the-probe audit program). In order to avoid performing multiple PEs and reduce QA costs, it is necessary to define an "acceptable" PE program and determine which SLT are performing these. NPAP would not have to include these sites within their PE network other than to establish some level of consistency/equivalency.
- 2) Combining NPAP and PEP Program- NPAP should be revised to a throughthe-probe audit approach, and with the possible use of STAG funding, the PM<sub>2.5</sub> PEP program could be enhanced to include NPAP.
- 3) Revising requirements for industry to contribute payments to NPAP- In the past, the NPAP, which was required under the PSD requirements, provided audits to industry for free. A mechanism for industry payment could be added to these requirements.
- 4) Updating guidance and practicability of the SRP. The SRP guidance has not been revised for a considerable length of time. Due to the stability of new ozone instruments, and the terminology (e.g., definitions of primary and transfer standards, etc.) that needs be revised, it is recommended that the SRP program guidance be updated.
- 5) Implementing PAMS audits prior to ozone season.- The PAMS audits should be scheduled from January to April or within some time frame that information could be evaluated and corrective actions take place prior to each ozone season.

## **5.3.11** Data Quality Assessments

A data quality assessment (DQA) is a statistical evaluation of a data set to establish the extent to which it meets user-defined application requirements (e.g., DQOs). Historically, DQAs have received little attention in the ambient air monitoring community. With a move towards performance-based measurements systems and DQOs., there will be more emphasis on DQAs. Recommendations include:

- 1) OAQPS responsibility for DQAs EPA-OAQPS should be responsible for the development of DQAs for all federally required data at the reporting organization level. Assessments at the site-specific level, or for objectives other than federal (i.e., non-trends speciation sites), would be the responsibility of the SLTs and be described in their QAPP.
- **2) Developing DQA tools** Similar to the PM<sub>2.5</sub> DQO software that is being modified as a DQA tool, as DQO development on the other criteria pollutants move forward, DQA tools will also be made available. It is anticipated that these tools would be integrated with AIRS.

#### 5.3.12. Data Validation/Verification

Similar to data quality assessments, there has not been much emphasis on data verification or validation techniques. Recommendations include:

- 1) Utilizing advancements in technology Earlier suggestions to increase the use of automated information transfer and quality control systems include the use of various automated data evaluation processes to provide for more real-time consistent screening and data verification/validation activities. Real-time data transfer technology would allow personnel at centralized offices to implement various verification/validation techniques, identify problems, and take corrective actions in a more real-time mode.
- 2) Developing and using validation templates The continued development of data validation templates, similar to the one developed by the PM<sub>2.5</sub> Data Validation Template Workgroup, would allow for some level of consistency across the ambient air monitoring program.
- 3) Validation programs on AIRS- The development of data verification/validation techniques on AIRS could be accomplished, but it may have a limited benefit if data do not get reported to AIRS for some considerable period of time.

# 5.4. Next Steps

The recommendations of the Workgroup are based on a concerted effort to identify, prioritize, and take action on the many aspects of the quality assurance program, so that changes are consistent with the overall Strategy's holistic review of air monitoring networks. To that end, the recommendations presented here should be considered preliminary, in that the Workgroup will be continuing its efforts through 2003. The Workgroup will likely need to enlist other volunteers to chair specific priority projects. Continuing participation by state and local agencies, under the auspices of STAPPA/ALAPCO, will help to assure a timely level of progress.

On a periodic basis, the progress will be reported to the NMSC. Once the final recommendations have been developed and the NMSC has determined consistency with the Strategy, a quality assurance final report will be prepared, and, once endorsed by the NMSC, will be implemented the basis of priorities, time frames, and available resources.

## Attachment 1

# Ambient Air Monitoring Quality System Activity Form

The following form was used by the QA Strategy Workgroup to identify and review the quality system activities related to the Ambient Air Monitoring Program. The Workgroup created a list separating the current QA activities into the three elements: 1) planning, 2) implementation, and 3) assessment/reporting. Each Workgroup member then selected one "Breakout Workgroup", based on the 3 elements/activities. Each Breakout Workgroup had a mix of Headquarter, EPA Region and SLT personnel. During Breakout Workgroup Conference calls, the Breakout Workgroup discussed the activity and completed the form. This information was reviewed during the Oct 23-25, 2001 QA Strategy Meeting in RTP, NC. The following Element/Activities can be found:

Element	Activity	Page
Planning	Systematic Planning	1
Planning	Regulation Development	4
Planning	Quality Management Plans	6
Planning	QA Project Plans & SOPs	8
Planning	Guidance Documents	11
Implementation	Training	13
Implementation	Data Verification/Validation	16
Implementation	Internal Quality Control	20
Implementation	Record Keeping	23
Assessment/Reporting	Site Characterization	26
Assessment/Reporting	Performance Evaluations	28
Assessment/Reporting	PSD network for NPAP	31
Assessment/Reporting	Technical Systems Audits	33
Assessment/Reporting	Data Quality Assessments	35
Assessment/Reporting	QA Reports	37
Assessment/Reporting	P & A Reports	39
Assessment/Reporting	Quality System Audits	41

Meeting Date: September 12, 2001

Agenda: Planning Activity I - Data Quality Objectives

Attendees: Dennis Mikel, Mike Papp, Terry Rowles, Alissa Dickerson, Melinda Ronca-Battista,

and Rachael Townsend

Quality System Element: Planning

Quality System Activity: Systematic Planning Process

Activity Description:

Quality System Activity: DQO Process, including gathering information on costs of different options, assessment of the impacts of options, evaluating their implications in terms of decisions, and writing and revising associated documentation at several iterations of the process.

Definitions: **Data Quality Objectives (DQO) Process** - A systematic strategic planning tool based on the scientific method that identifies and defines the type, quality, and quantity of data needed to satisfy a specified use. DQOs are the qualitative and quantitative outputs from the DQO Process.

**Data Quality Objectives (DQOs)** — The qualitative and quantitative statements derived from the DQO Process that clarify study's technical and quality objectives, define the appropriate type of data, and specify tolerable levels of potential decision errors that will be used as the basis for establishing the quality and quantity of data needed to support decisions.

When the DQO Process is not applicable (i.e, the objective of the program is estimation, research, or any other objective that does not select between two opposite criteria), a systematic method for defining performance criteria must be used.

## Activities covered under this description:

- This element applies to all data collection activities, although the EPA's graded approach to QA allows simplified DQO processes for small data collection activities. Current DQO guidance does not, however, adequately delineate those cases when a simplified DQO process can be used and what would be acceptable for such a simplified process. The only exception is for training or demonstration projects, where the data will not be used for any purpose. In these cases, the use of the equipment is the point of the exercise.
- The national program of data collection and analysis for the purpose of comparing to the NAAQS requires a rigorous DQO process for all pollutants for which there is a standard. This effort must come from OAQPS and should be completed as soon as possible.
- < Tribe, State and local agencies should retain the flexibility to develop their own DQOs.

However, DQOs for data used to compare to national standards may continue to be used as de facto allowable bias, precision and LLD values in those cases when data may eventually be used to compare to national standards. Because of this, and for EPA to adhere to its own written policies, it is imperative that OAQPS fund and complete the DQO process for all criteria pollutants.

- The DQO process may result in performance specifications, rather than equipment specifications. This will increase flexibility and may reduce overall costs.
- < Metadata guidance should be prepared, so that all data incorporated into national or regional estimates from different organizations has associated information such as precision, bias, and LLD.
- Resources and funding from both EPA OAQPS and EPA Regions should be provided to Tribal, State, and local agencies in the form of training and contract support for these agencies to develop DQOs.

# What is the activity's function or use:

To ensure that the data are appropriate to be used for the objectives of the data collection effort.

Is there a product? Who is the major user of the product or information:

The product is documentation in the form of a QA Plan or manual that includes Data Quality Objectives and other sections that were prepared using EPA guidance. The user is anyone who uses that data for any purpose.

## Brief description of current activities:

- < Tribe, State, and local agencies develop DQOs now, usually using guidance from EPA. EPA-funded projects receive different levels of technical review, due to differences among EPA regions and different priorities for different individuals.</p>
- < Tribe, State, and local agencies comply with extremely specific requirements for PM2.5 measurements, while other criteria pollutants, for which no national DQOs were developed, are measured without the same level of consistency in detail.</p>

#### Who is responsible for the activity (currently):

< OAQPS is responsible for developing DQOs for Federally required data. Tribes, State, and local agencies are responsible for developing their own DQOs for other data uses.

## Is the activity important? (what does it get us):

The DQO process, whether simplified or extensive, is mandatory to ensure the data can answer the questions being asked. In addition, knowing the quality of the data allows users to determine if other, un-anticipated questions, can be answered by the data. Without measured

quality in terms of bias, precision, and LLD the data may be easily misused.

Pros and Cons of the activity as it's currently implemented:

Pros: - Significant flexibility for Tribe, State, and local agencies, except for PM2.5, which is extremely prescriptive.

- Improved compatibility of objectives and measurement methods.

Cons: - Inconsistency among Tribe, State, and local agencies for small-scale projects.

- Potential misuse of data.

# Ways of improving the activity:

- < OAQPS needs to develop DQOs for the NAAQS. In addition, there should be a project to evaluate converting the DQOs for PM2.5 to include performance-based standards.
- < Complete DQOs for other criteria pollutants. Prioritize this activity to ozone and toxics (if necessary). If a coarse particulate matter standard is coming along, get ahead of the curve for this DQO.</p>
- < Link DQOs more directly to Federal Reference Method and Equivalency Program
- Use of a graded approach to QA Not all ambient air monitoring data are used for comparison to the NAAQS. Therefore some monitoring objectives may not call for quality systems and quality assurance documentation (QAPPS) to meet the stringent requirements for NAAQS comparison purposes
- < Provide more ambient air specific training on the DQO process
- < Funding should be provided to Tribe, State, and local agencies to develop DQOs
- < Provide a vehicle for statistical support on DQOs. OAQPS will establish a contract vehicle that would allow SLTs to tap into statistical help as it relates to DQOs.

Who should be providing (responsible for) this activity?

- < All Tribe, State, and local agencies can develop their own DQOs; however, it is incumbent upon a national organization such as OAQPS to develop the national DQOs.
- In order that DQO development be adequately conducted by tribes, states, and locals, the EPA should provide adequate resources. These would include at least Level of Effort contracting for DQO development assistance and training in DQO development specific to air programs.

Does it require changes to regulation or guidance?

Both regulation and guidance should be changed to reflect

- 1. the DQOs developed by OAQPS for criteria pollutants, and
- 2. performance-based DQO statement for PM2.5 and other pollutants as an alternative acceptable approach to ensuring adequate data quality.

Meeting Date: September 26, 2001

Agenda: Planning Activity II - Regulation Development

Attendees: Mark Shanis, Terry Rowles, Chris Hall and Rachael Townsend

Quality System Element: Planning

Quality System Activity: Regulation Development

Activity Description:

Quality System Activity: Writing, presenting, and revising regulations that specify how the air quality measurements must be made in order to conform to the assumptions made in the DQO process and produce results of the type and quality needed by the decision makers.

Definition:

Portions of 40 CFR 58 Appendix A, which include:

- 1. General Information
- 2. Quality System Requirements
- 3. Reporting
- 5. Calculations

Activities covered under this description:

< Writing, presenting, and revising regulations that specify how the air quality measurements must be made, analyzed, and reported.

What is the activity's function or use:

< Codify the specifics of quality systems nation wide.

Is there a product? Who is the major user of the product or information:

< Guidance and requirements in 40 CFR that guide quality systems.

Brief description of current activities:

< EPA takes the initiative, review through STAPPA/ALAPCO, proposed for CFR, then promulgated.

Who is responsible for the activity (currently):

< EPA (OAQPS) and designees.

Is the activity important? (what does it get us):

< Important and required.

Pros and Cons of the activity as it's currently implemented:

Pros: - consistency

Cons: - costly and time consuming to implementers

Ways of improving the activity:

- Revision of 40 CFR 58 App. A. and Combine Part 58 Appendix A and B- Since most of the requirements for Appendix A (SLAMS) and Appendix B (PSD) are the same, the Workgroup agreed that the appendices could be combined.
- < Address how the regulation process will be affected including the DQO process.
- < DQOs are not addressed in the CFR (guidance or required; at what level is it required or appropriate?).
- Review the requirements, focusing on the "musts" If performance based measurement systems were going to work, performance goals (DQOs) were needed and that quality control (QC) samples would be used to evaluate the achievement of the goals. However, the frequency of implementing the requirements and some of the actual acceptance criteria may not be required in CFR. These specifics would be included in guidance documents. Therefore, organizations with sophisticated QA programs would have the flexibility to develop their quality systems with minimal hindrance in requirements while organizations that had less sophisticated programs or expertise could use the guidance to develop their quality systems.
- Ensure CFR clearly discriminates between requirements and what is guidance; this is made more confusing when guidance documents are referenced in the CFR as a requirement.
- < Adjust regulation for guidance on how and when organizations can collapse QMP and QAPP.
- < Identify methods to develop the guidance for small organizations and projects, such as those who can collapse the QMP and QAPP.
- < The graded approach need to be addressed in the CFR, including specific criteria for different levels of QAPPs with examples.
- Develop a tool to identify each requirement, provide management with use and value information, and access the requirement within the regulation development process to make modifications useful to management during the process. (During processing and development of regulations, include tools for management to understand and ensure communication with technical staff on how it relates to their job. Make sure management have understanding on how to use and importance.)
- < Revise CFR to provide for quarterly data certifications

Who should be providing (responsible for) this activity?

< EPA (OAQPS), assisted by affected organizations among Tribes, States, and local agencies.

Meeting Date: September 19, 2001

Agenda: Planning Activity II - Regulation Development (discussion to continue Sept. 26)

(See the attached excerpts from 40 CFR Appendix A with

requirements highlighted.)

Planning Activity III - Quality Management Plans

Attendees: Norm Beloin, Mike Papp, Terry Rowles, Alissa Dickerson, Melinda Ronca-Battista,

and Rachael Townsend

Quality System Element: Planning

Quality System Activity: Quality Management Plans

Activity Description: Defining and requiring content for QMPs.

Definition: Quality Management Plan (QMP) — A formal document that describes the quality

system in terms of the organization's structure, the functional responsibilities of management and staff, the lines of authority, and the required interfaces for those

planning, implementing, and assessing all activities conducted.

Activities covered under this description:

< Defining and requiring content for QMPs.

What is the activity's function or use:

- < defines the quality system for the entire organization
- < provides a description of the organization and its mission
- < describes the organization's management responsibilities
- < helps ensure consistency between programs within the organization
- < serves as an audit tool

Is there a product? Who is the major user of the product or information:

< QMP guidance published by EPA's Office of Environmental Information, in the form of guidance document EPA QA/R-2 (August 1994); note that this was revised in the spring of 2001 but the changes were very minor (EPA/240/B-01/002). QMPs are developed and revised by most larger monitoring organizations.

Brief description of current activities:

- < Revisions to EPA QA/R-2 are not scheduled.
- < Revisions to QMPs by Tribal, State, and local organizations.

Who is responsible for the activity (currently):

< EPA's OEI and/or OAQPS, in terms of issuing guidance for QMPs, and the organizations themselves who write and use their own QMPs.

Is the activity important? (what does it get us):

 valuable to organization, particularly States and other large monitoring organizations; see bullets above.

Pros and Cons of the activity as it's currently implemented:

Pros:- see bullets above

Cons:- QMPs are often not distributed to all staff

- **S** no guidance on when the QMP and QAPP can be combined into one document(for smaller organizations)
- **S** no clear guidance on how to ensure independence of QA review in small organizations
- **S** no clear guidance on the use of the graded approach
- **S** no resources are available in many organizations for QMP preparation

Ways of improving the activity:

- Increase consistency between EPA Regional offices on how they review QMPs.
- < Revise EPA QA/R-2 with the substantive changes discussed here.
- < Define needs for QMPs for all agencies.

Who should be providing (responsible for) this activity?

< EPA's OEI or a separate document from OAQPS with assistance from affected organizations.

Does it require changes to regulation or guidance?

< Yes, changes to EPA QA/R-2 or the issuance of a separate document is required.

Meeting Date: September 26, 2001

Agenda: Planning Activity IV - QAPPs and SOPs

Attendees: Terry Rowles, Melinda Ronca-Battista, Dennis Mikel, Alissa Dickerson,

Rachael Townsend

Quality System Element: Planning

Quality System Activity: QA Project Plans and SOPs

Activity description: Requiring and specifying content for QAPPs and SOPs.

Activities covered under this description:

Definition: Quality Assurance Project Plan (QAPP) — A formal document describing in comprehensive detail the necessary QA, QC, and other technical activities that must be implemented to ensure that the results of the work performed will satisfy the stated performance criteria..

**Standard Operating Procedure (SOP)**-A written document that details the method for an operation, analysis, or action with throughly prescribed techniques and steps, and that is officially approved as the method for performing certain routine or repetitive tasks.

What is the activity's function or use:

< Guidance for QAPPs is used by Tribe, State, and local agencies to understand and adhere to the EPA requirements.

Is there a product? Who is the major user of the product or information:

EPA QAPP guidance is used by Tribe, State, and local agencies to develop their required QAPPs, as well as EPA regions in their review of submitted QAPPs. Note that the QAPP guidance document (QA/R-2) was revised in the spring of 2001 but only very minor changes were made (EPA/240/B-01/002).

Brief description of current activities:

No work is now being conducted by OAQPS or the EPA OEI to prepare or revise guidance for QAPPs.

Who is responsible for the activity (currently):

< OAQPS is the only entity that has the jurisdiction and resources for revising or producing air

monitoring-specific QAPP guidance.

Is the activity important? (what does it get us):

Revising the QAPP guidance is very important. As it now stands, Tribe, State, and local air departments, especially those in small organizations, are often put in the position of either hiring contractors to produce the statistical evaluation of DQOs or copying DQOs from other groups or projects. Both of these options often produce QAPPs which are not helpful. Revising the current QAPP guidance will bring increased respect for and use of QAPPs and DQOs as sensible, integrated parts of the project. As DQO development becomes a common element of QAPPs, related issues may require changes in QAPP guidance.

Pros and Cons of the activity as it's currently implemented:

Pros: - The model PM2.5 QAPP is thorough and widely used.

**S** The general QAPP guidance is useful for large-scale projects for large organizations.

Cons: - The QAPP guidance does not include provision for small organizations, or for those projects for which a statistical treatment of DQO options is not relevant.

Ways of improving the activity:

Current guidance for QAPPs and SOPs should be modified as follows:

- < Guidance should be provided for those cases when a new statistical derivation of DQOs is not necessary, for example, when a Tribe, State, or local organization is using DQOs already developed by OAQPS for the NAAQS, or when extremely simple conclusions are to be drawn from the results. This guidance should provide clear and simplified treatment of the statistics of DQOs, such as that provided for radiological measurements in the Multi-Agency Radiological Survey and Site Investigation Manual (MARSSIM, downloadable documents at: www.epa.gov/radiation/marssim/). A decision tree to facilitate the choice of options would be useful.</p>
- < Develop a generic QAPP Take the G-5 EPA QAPP Guidance and develop a generic ambient air monitoring QAPP software product that would allow the SLTs to input the correct information into each section for their particular monitoring program</p>
- < As part of reference method designation process, make vendors develop adequate SOPs that could be made available for monitoring agencies to modify.
- < Guidance to EPA regions on the need for consistency in the review of QAPPs should be issued as soon as possible. Regions now differ widely on their priorities and expectations regarding QAPPs, and this adds confusion and delay to the project approval process.</p>
- < Guidance for QAPPs should clearly state that QAPPs that are for projects covered by a QMP do not need to duplicate information in the QMP or applicable SOPs.

Who should be providing (responsible for) this activity?

< OAQPS is the only entity that can initiate this activity.

Does it require changes to regulation or guidance?

< Guidance should be modified or a second QAPP guidance document issued.

Meeting Date: October 4, 2001

Agenda: Planning Activity V - Guidance Documents, such as Network Design and Technical

Methods

Attendees: Chris Hall, Dennis Mikel, Mike Papp, Norm Beloin, Alissa Dickerson, and Rachael

Townsend

Quality System Element: Planning

Quality System Activity: Guidance Documents, such as Network Design and Technical

Methods

Activities described: Researching, writing, revising, and obtaining approval for guidance that assists those trying to adhere to the requirements of the regulations. Documents provide non-mandatory information including examples.

## Activities covered under this description:

< Writing of new guidance documents, technical methods and network design

- The red books and methods associated with the red books
- < Guidance documents on siting criteria

# Activities not being done:

- < Data quality assessment guidance
- < Data validation guidance
- < Data acceptance guidance
- < Guidance on what level of quality is needed for AQI decisions (real -time-data)

## What is the activity's function or use:

- < Help define/expand regulations
- < Should provide a strongly recommended way of doing the work
- < Clarify what is required in the regulation
- < Provide some consistency across the nation for monitoring programs

## Is there a product? Who is the major user of the product or information:

< Guidance documents and technical documents, including new methods are used by Tribal, State and local agencies as well as data users, like health effects users.

Brief description of current activities:

- < Siting guidance
- < Production of guidance documents
- < Documents are reviewed periodically

Who is responsible for the activity (currently):

< EPA (OAQPS)

Is the activity important? (what does it get us):

< Same as function of activity stated above.

Pros and Cons of the activity as it's currently implemented:

Pros: - Pro-active approach to upgrading these documents

Cons: - Have not had enough time to work on; a number of guidance documents are outdated.

- **S** Don't have formal program to review relevance of guidance
- **S** No single way to access all of the guidance documents

Ways of improving the activity:

- < Need more state and local involvement during the early development.
- < State and locals need to have a full time person for QA for the air monitoring programs.
- < Define or clarify attributes or responsibilities of QA person or manager.
- < Get more state and locals in on which documents are more important to them, to prioritize which are more important to them to get revised and updated.</p>
- < QA forum for continued support and exchange of information.
- Combining all guidance into one document It was suggested that the QA Handbook Volume II (Redbook) be the home for the various guidance.

Who should be providing (responsible for) this activity?

< EPA Headquarters

Does it require changes to regulations?

< No, except for 40 CFR Part 58, App. A, Section 2.2 which states that PAMS must be consistent with EPA guidance.

Meeting Date: September 12, 2001

Agenda: Implementation—Training

Attendees: Tom Parsons, Donovan Rafferty, Jerry Sheehan, Andy Johnson, Rayna Broadway,

Anna Kelly, Mark Shanis, Mike Papp

Quality System Element: **Implementation** 

Quality System Activity: **Training** 

Activity Description:

Definition: None

Actions covered under this description:

- < Sampling equipment or measurement device operation, calibration and maintenance
- < Laboratory analysis calibration
- < Sample chain of custody, preparation, analysis, archiving
- < Quality assurance activities performance evaluation, auditing, data quality assessment
- < Information manager

What is the function or use of this activity?

< Ensure that a consistent methodologies are followed that allows for the collection of data of acceptable quality.

Is the activity important?

< Yes- Provides some assurance of data comparability within and between monitoring organization and allows for the transfer of knowledge and experience

Is there a product?

< Yes-More experienced staff and data of acceptable quality

Is this a new activity?

No.

Brief description of current activities

< On the job training - SLT one-on-one or group training

- < Regional training (NESCAUM, MARAMA, WESTAR, TAMS)- various training activities put on by regional organization.
- < Air and Waste Management Association (AWMA)- training put on a national or specialty conferences
- < Vendor training training put on by vendors which can be incorporated into the purchase of equipment.
- < Air Pollution Distant Training Network (APDLN) provide remote televised training which also allow for real-time questions
- < Air Pollution Training Institute (APTI)
- < Redbook (self instruction)
- < The web sites, especially AMTIC

Who is responsible for the activity-

< The responsibility for training occurs at all levels.

Pros and Cons of the activity as it's currently implemented:

- Pros On the job training is probably the most important training technique. Some SLT have good training programs
  - -APDLN for  $PM_{2.5}$  was successful at providing a good general level of training for the program.
- Cons Training is not mandatory so some people do not take training when it would be advantageous
  - ! Funds are not always available remote training if it is needed
  - ! When SLT resources are tight training is one of the first things to be cut
  - ! Although on the job training has advantages, the downside is there's not much standardization in that process and a newer agency or one that has lost its core personnel to attrition can't count on OJT.

Ways of improving the activity:

- < Develop web- based training courses
- < Place some important training in regulation
- < Development of some type of Ambient Air Monitoring Training Certification Program for:
  - ! Upper Management
  - ! Ambient Air Monitoring Manager-
  - ! Site Operator
  - ! Calibrators
  - ! QA Manager
  - ! QA Technician
  - ! Laboratory Scientist
  - ! Information Manager

- < Tie career growth to training
- < Try to include vendor training as part of equipment purchases
- < Combining all guidance into one document. Revise the Redbook.
- < Annual QA Conference The workgroup suggested that a QA meeting be held annually (similar to the AIRS Training). It was suggested that this QA meeting coincide with the National QA Conference in order to take advantage of the training modules put on by EPA Quality Staff at the National Meeting.</p>
- < Recognize that QA within a state agency may have more than one training need

Does is require changes to regulation or guidance

# Regulation:

- < Need to decide if certain training should be requirement.
- < May include in regulation that training is important and records should be kept of training.

## Guidance:

< May want to improve Redbook guidance on training to include certification proposal.

Meeting Date: September 20, 2001

Agenda: Implementation—Data Verification/Validation

Attendees: Tom Parsons, Rachael Townsend, Donovan Rafferty, Rayna Broadway, Anna

Kelly, Mike Papp

Quality System Element: Implementation

Quality System Activity: Data Verification/Validation

Activity Description:

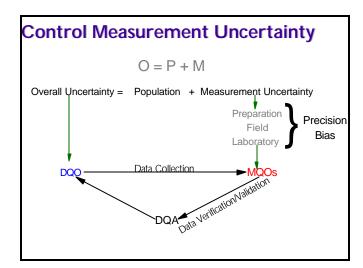
Definition:

**Verification** - Confirmation by examination and provision of objective evidence that specified requirements have been fulfilled. In design and development, validation concerns the process of examining a result of a given activity to determine conformance to the stated requirements for that activity. (ANSI/ISO/ASQC A8402-1994).

**Validation**- the process of substantiating specified performance criteria. confirmation by examination and provision of <u>objective evidence</u> that the particular requirements for a specific intended use are fulfilled. (ISO 8402)

# Actions covered under this description

- < Verification of data entry (100% checks, double entry techniques etc.)
- < Using QC information to determine the validity of samples.
- Using range checks or internal consistency checks to determine erroneous data.
- < Using automated flagging and data quality systems to identify outliers or erroneous data for possible invalidation



What is the function or use of this activity?

The figure can be used to illustrate where validation occurs. DQOs are developed that define the acceptable overall data uncertainty. Measurement quality objectives are developed that help assure that activities occurring at various phases of the measurement process (field, lab etc.) Maintain an acceptable level of data quality. Therefore the MQOs are identified as the various QC samples or QC activities

undertaken to "ensure " the DQOs are met. Data verification/ validation is the process of taking this information to ensure that data of unacceptable quality is identified and appropriately handled so that it cannot effect the decision making process.

Is the activity important? (what does it get us)

< YES

Is there a product? Who is the major user of the product or information

The "final" product is data of acceptable quality in a final data base. The major user of the QC data are the quality assurance personnel who need this "meta-data" to help determine data validity.

Is this a new activity? What activity does it replace or enhance?

< No, this is not a new activity. It does not replace any activity; it enhances the usefulness of the resultant data.

Brief description of current activities

- < In general, the current activity is very similar among most SLTs. Various quality control information is required or suggested to be collected during monitoring activities. These include:
  - ! zero/span checks
  - ! weekly/biweekly precision checks
  - ! Collocated precision
  - ! equipment stability information (flow, temp pressure)
  - ! shelter or laboratory information (temp, humidity etc.)
  - ! Contamination information (field notes, field/trip/lab blanks)
  - ! performance evaluations
  - ! calibration information
  - ! field notes (sampler issues, damage, contamination etc)

However how this data is used in the validation process may differ among SLTs.

< Once the data is entered to AIRS there is additional QA reports that are run that can also help in the final validation of data.

Who is responsible for the activity (currently).

< SLTs

Pros and Cons of the activity as it's currently implemented:

- Pros! Some organizations have developed procedures for the consistent verification/validation of data
  - ! Real time data reporting has helped to initiate verification/validation screening tools. Although these tools do not provide full validation of data, they do provide an early review of information.
  - ! The PM<sub>2.5</sub> Data Validation Template helped provide some consistency in data verification validation among SLTs
- Cons There is no consistency in data verification/validation techniques among SLTs.
  - ! Local site information could be very helpful in the validation process (events) but in many cases this information is not recorded and therefore not available.
  - ! Resources in some SLTs not available for timely validation
  - ! Present verification techniques taking too long, meaning corrective action is not taken as soon as possible.
  - ! Due to the diverse use by SLTs information management systems, there is currently no easy way to develop automated validation techniques (at a headquarters level) in a cost effective manner.

## Ways of improving the activity:

- < Technology is available for more real time validation that could free up resources for other activities: This could start with:
  - ! Use of data logging, telemetry or "lease-lines" to get data into information management systems and validation systems more quickly.
  - ! Use of computer technology by the site operator to access data that has been reviewed at the "central office" in order to implement corrective actions in a more real time mode
  - ! Use of the new AIRS system to develop more data assessment/validation techniques that could then be consistently used by all SLTs.
- < Continue the development of Validation Templates for the other criteria pollutants
- < Development of QA/QC evaluation reports The Workgroup suggested the generation of various validation/evaluation program and reports (on AIRS or standalone) to reduce the burden on data validation personnel and provide for quicker data certification.
- < Certified/uncertified data flagging Data qualifiers are not used for the majority of the SLAMS pollutants, meaning that SLT personnel wait for data to be validated before uploading to AIRS. Since many SLTs use data qualifiers on their local sites to inform data users that the real time data is not validated, maybe AIRS data could be initially uploaded as "unqualified" and on a quarterly basis, based on suggestion above, have this qualifier removed. This would allow OAQPS to develop generic data evaluation/validation reports (see below) on AIRS that could be used/or modified by the AIRS user community rather than having SLTs develop their own reports.</p>

Who should be providing (responsible for) this activity?

# < SLTs

Does this require changes to regulation or guidance?

- < If data validation is tied to performance (DQOs) process (see figure) then some regulations changes may occur if QC criteria are changed or removed.
- < Guidance in Redbook could be changed to reflect validation templates

Meeting Date: October 9, 2001

Agenda: Implementation—Internal Quality Control Activities

Attendees: Tom Parsons, Donovan Rafferty, Jerry Sheehan, Andy Johnson, Rayna Broadway,

Anna Kelly, Mark Shanis, Mike Papp

Quality System Element: **Implementation** 

Quality System Activity: Internal Quality Control Activities

Activity Description:

Definition: the overall system of technical activities whose purpose is to measure and control the

quality of a product or service so that it meets the needs of users. The aim is to provide quality that is satisfactory, adequate, dependable, and economical.

# Actions covered under this description

< See Redbook Measurement Quality Objective Forms (Appendix 3 in Redbook)

- < Zero/Span checks
- < Accuracy audits
- < Verification checks (flow rate, temp, pressure, time)
- < Calibrations
- < Recertifications (SRP program, primary standards and transfer standards) gases, other QC instruments
- < Precision checks (automated and collocated)
- < Detection limit tests
- < NPAP/State Audits (may also be included under performance evaluation)
- < Routine instrument maintenance

What is the function or use of this activity?

Ensure sampling, measurement equipment, or environmental monitoring conditions (shelters, labs) are operating within acceptable ranges to produce data of know and acceptable quality.

Is the activity important? (what does it get us)

Yes quality control activities provide data users with checks at enough frequency to maintain "control" over data quality at various phases (sampling, preparation, analysis) of the measurement process. Is there a product? Who is the major user of the product or information

In most case there is not a product other than routine data of acceptable quality. However, some of the major quality control samples are reported to AIRS and can be used to provide a measure of precision and bias for reporting agencies. Products such as control charts etc. can also help to document data of acceptable quality.

Is this a new activity? What activity does it replace or enhance?

< No it's not a new activity

Brief description of current activities

< Activities defined in Redbook

Who is responsible for the activity (currently)

< In most case State/local/Tribes are responsible for these activities

Pros and Cons of the activity as it's currently implemented:

- Pros- The current QC check requirements and guidance do seem to provide an adequate evaluations of data quality
- Cons! Some organizations may feel "audited to death". There may be some redundancies with our various auditing activities such as NPAP, State and internal auditing functions
  - ! Some QC checks have "lost there value" due to the improvements of monitoring technology.
  - ! Reducing frequencies of some checks may have the potential for invalidating more data.

Ways of improving the activity:

- < Automate measurement systems as much as possible. Providing state of the art measurement, data logging/data transfer and QC systems will provide coast savings in the long run and provide for QC at higher frequency at no additional cost.</p>
- < Automate zero/span Some organizations may still be performing these manually and at less frequency than recommended.
- < Through-the-probe zero/span/precision checks have checks cover entire inlet/manifold systems</p>
- < Develop QC checks based on system performance. Some checks, due to better, more stable equipment may not need to be checked as frequently as required or suggested.
- < Have vendors of new instruments be required to develop adequate SOPs as part of the reference and equivalency process (may need to be added to SOP form).

Who should be providing (responsible for) this activity?

< State/local/Tribal monitoring agencies will maintain responsibility for this activity.

Does is require changes to regulation or guidance?

 Unsure at present- a thorough review of QC requirements in CFR and guidance should be implemented. Meeting Date: October 16, 2001

Agenda: Implementation—Record Keeping

Attendees: Tom Parsons, Andy Johnson, Don Gourley, Anna Kelly, Mike Papp

Quality System Element: Implementation

Quality System Activity: Record Keeping

Activity Description:

Definition: a written, documented group of procedures describing required records, steps for

producing them, storage conditions, retention period and circumstances for their

destruction or other disposition.

Actions covered under this description

Storage of pertinent ambient air monitoring program documents and records at State/local/Tribal organization, EPA Regions and Headquarters.

What is the function or use of this activity?

To document or provide supporting documentation of the quality/validity of ambient air monitoring data and adherence to ambient air monitoring requirements.

Is the activity important? (what does it get us) - YES

- c provides for a repository of pertinent program information.(current and historical)
- < provides documentation of data validity

Is there a product? Who is the major user of the product or information

< Products are the records/documents. The user is the organization collecting the information and potentially organizations required to review the records during auditing activities or challenges to the data validity.

Is this a new activity? What activity does it replace or enhance?

< No, not a new activity.

Brief description of current activities.

Workgroup used Section 5 "Documentation and Records" of the Quality Assurance Handbook for Air Pollution Measurement Systems (Volume II Part 1) as a source of information on this subject. The table below, which is in the section, was reviewed to determine whether the categories and record types were appropriate and comprehensive.

Categories	Record/Document Types	
Management and Organization	State Implementation Plan Reporting agency information Organizational structure of monitoring program Personnel qualifications and training Quality management plan Document control plan Support contracts	
Site Information	Network description Site characterization file Site maps/pictures	
Environmental Data Operations	QA Project Plans Standard operating procedures (SOPs) Field and laboratory notebooks Sample handling/custody records Inspection/maintenance records	
Raw Data	Any original data (routine and QC)	
Data Reporting	Air quality index report Annual SLAMS air quality information Data/summary reports Journal articles/papers/presentations	
Data Management	Data algorithms Data management plans/flowcharts	
Quality Assurance	Control charts Data quality assessments QA reports System audits Network reviews	

A number of points were made during the discussions;

- < Some organizations have data archive requirements for much longer than the statute of limitations described in Section 5 of the Redbook (3 years).
- < It appeared that resources needed for records archive and storage were adequate.
- The Breakout Group felt the table sufficiently covered the records and document types for the ambient air monitoring program. However certain records (i.e., record types in management and organization) may be the responsibility of management levels outside the monitoring organization.

< A monitoring organization may be responsible for data collection activities implemented by organizations outside of the immediate office (contractors or other local organizations). We may need some additional guidance on what would need to be archived.</p>

Who is responsible for the activity (currently)

< organizations responsible for ambient air data collection activities

Pros and Cons of the activity as it's currently implemented:

Pros-

Cons! some organizations may not have a central filing capability. Therefore, individuals are filing and archiving information for which they are immediately responsible. During personnel turnover there is a possibility that this information gets discarded.

**NOTE**: This situation occurred with the CY2000 PM2.5 network where a significant amount of QC data disappeared when a site operator was removed from his/her position

There may be discrepancies within organizations documentation (QMP/QAPPS/PPG) with regards to record keeping. Monitoring organization must ensure there is consistency among these various documents.

Ways of improving the activity:

- Centralize filing systems it appeared that organizations are moving in this direction.
- < Review Table 5-1 in Redbook- ensure agreement on record types.

Who should be providing (responsible for) this activity?

< Organization dependent.

Does it require changes to regulation or guidance?

< No change in regulation; may be modification to guidance

#### Other issues:

< Need to check on the defensibility of electronic data.

Meeting Date: September 13, 2001

Agenda: Assessment/Reporting -Site Characterization

Attendees: Mike Miguel, Michael Papp, Mark Shanis, Richard Heffern

Quality System Element: Assessment/Reporting

Quality System Activity: Site Characterization

**Activity Description** 

Definition: Applicable siting criteria for SLAMS, NAMS and PAMS are specified in 40 CFR Part 58 Appendix E. The on-site visit itself consists of the physical measurements and observations needed to determine compliance with the Appendix E requirements, such as height above ground level, distance from trees, paved or vegetative ground cover, etc

What is the function or use of this activity?

< The function of the site characterization is to ensure national uniformity of parameter specific air monitoring activities.

Is the activity important? (What does it get us)

< Yes, the activity is important and it allows one to determine if the network conforms to the regulations.

Is there a product? Who is the major user of the product or information?

< Yes, there is a product (report) and all levels of government use the information.

Is this a new activity? What activity does it replace or enhance?

< No, it enhances the overall consistency of air monitoring data.

Brief description of current activities.

States/local conduct site evaluations of their air monitoring networks once a year. The Regions usually conduct site evaluations during a technical system audit and only conduct a percentage (5%) of a air monitoring network.

Who is responsible for the activity (currently).

< OAQPS, Regions and States are responsible for this activity.

Pros and Cons of the activity as it's currently implemented:

Pros:! Aids the Regions and State/local to evaluate the air monitoring networks.

- ! Provides uniformity
- ! Some states have a Website for current site activities.

Cons! No consistent documentation of site evaluations

- ! Most States do not have a website for current site activities.
- ! No consequences for not conducting site evaluations ( No comparison between AIRS an hard copy in the files)

Ways of improving the activity:

- Conduct polls of the Regions and State/locals on who is conducting site evaluations.
- < Setting minimal levels and tracking review the requirements for the frequency of such characterization and recommend a change (if necessary).
- Ensure better tracking of this information to ensure they are being performed. AIRS has an area that can be used for this tracking activity.
- Ensure updates made in AIRS Information from inspections (monitors or sampling equipment added to site, Lat/Long changes) that reflect a needed change in the site record in AIRS are not always getting revised. There needs to be some method of ensuring information found during site characterization gets corrected in AIRS in a timely manner.
- Verify the control of the control
- < Site characterization training- It was suggested that a training module be developed for the performance of site characterizations.
- Speed up approvals for discontinuing sites- SLTs submit paperwork for discontinuing sites that do not get approved for a considerable length of time. OAQPS needs to review this process

Who should be providing (responsible for) this activity.

The Regions and the States should be responsible for this activity.

Does this require changes to the regulation or guidance?

< No

Meeting Date: September 26, 2001

Agenda: Assessment/Reporting - Performance Evaluations

Attendees: Danny France, Matt Plate, Mark Shanis, Mike Miguel, Richard Heffern, Rayna

Broadway, Vic Guide, Rachael Townsend, Scott Hamilton

Quality System Element: Assessment/Reporting

Quality System Activity: **Performance Evaluation** (NPAP, PEP, Ozone Verification)

Definition: a type of audit in which the quantitative data generated in a measurement system are obtained independently and compared with routinely obtained data to evaluate the proficiency of an analyst or laboratory.

What is the function or use of this activity?

< To ensure the quality of data collect and resolve any significant quality assurance problems.

Is the activity important? (What does it get us)

The activity is important. It allows for the intercomparability of data sets and identification of problem areas.

Is there a product? Who is the major user of the product or information.

< Uniform data on a national level. All levels of the government/tribes and industry are major users of this information.

Is this a new activity? What activity does it replace or enhance?

< No. The performance evaluation program enhances the overall quality system on the nation's air monitoring program.

Brief description of current activities.

< State/locals and PSD networks participate in the NPAP and PEP. Most tribal agencies do not participate in the programs.

Who is responsible for the activity (currently)?

< OAQPS, Regions and States are responsible for the activity.

Pros and Cons of the activity as it's currently implemented.

Pros:! It enhances the overall consistency of air monitoring data.

! Some states like the program as it is.

Cons: Very little return for the VOCs and Carbonyl for the PAMS.

- Some states have such small air monitoring programs it is impossible to have adequate separation QA and monitoring staff. In this case, independence is not achieved.
- ! To much duplication in the program.
- ! Need more flexibility in the program.
- ! Regulatory guidance in certifying ozone transfer standards is 20 years old.

# Ways of improving the activity:

- < PAMS NPAP should be conducted in the January to March time frame so that potential problems can be rectified prior to the ozone season.
- < Less compounds could be included in the PAMS NPAP audits. Participants would prefer if higher quality standards (NIST) are utilized with less compounds.
- It was suggested that ambient air comparisons be used to compare between lab results. This is already being done at some Regions.
- < Headquarters should certify auditors for parameters. This is being done for PM2.5.
- < Eliminate duplication in the NPAP program. EPA could certify States that do have a PE program in place, conduct round robin with labs.
- < Combining NPAP and PEP Program- Revise NPAP to a through-the-probe audit approach. STAG funding mechanism of the current PM<sub>2.5</sub> PEP could be enhanced to include NPAP.
- Revise requirements for industry to contribute payments to NPAP- In the past, the NPAP, which was required under the PSD requirements, provided audits to industry for free. It was suggested that a mechanism for industry payment could be added to the requirement
- The current regulation require transfer standards to undergo a 6-certification at the beginning of each ozone season (provided the previous 6-days certification lapsed) and then a 1-day recertification at the end of 90 days. This poses a problem in some areas which have to ship ozone standards. The current frequency may be overkill. The group commented that this would depend on the situation. For example, if a reporting organization was experiencing discreprencies or other QA/QC problems, the frequency may need to be increased so that the problem could be resolved. Conversely, if a reporting organization was running smoothly with audits, calibrations and span checks showing expected results, then this frequency may be too much. The group concluded that the 90-day frequency seems to be appropriate but is subjective.
- Update guidance and practicability of the SRP. The SRP guidance has not been revised for a considerable length of time. Due to the stability of new ozone instruments, and jargon (definitions of primary and transfer standards etc.) that needs be revised, it was felt that the SRP program guidance needed updating.
- < PM2.5 PEP comments: Alaska commented that the PEP auditor need to space out audits throughout the year. It was suggested that the quarterly audits may be too many. The

frequency of could be determined by the success (or failure) of the previous audit.

Who should be providing( responsible for) this activity?

< OAQPS, Regions and the States should be responsible for this activity.

Does the activity require changes to regulation or guidance?

< Current regulatory guidance used in certifying ozone transfer standards may need to change.

Meeting Date: October 10, 2001

Agenda: Assessment/Reporting - PSD networks participation in NPAP

Attendees: Danny France, Matt Plate, Mark Shanis, Michael Papp, Mike Miguel

Scott Hamilton, Richard Heffern, Rayna Broadway

Quality System Element: Assessment/Reporting

Quality System Activity: PSD networks participation in NPAP

What is the function or use of this activity?

< The function of the PSD networks participation in the National Performance Audit Program is to ensure that the ambient air data collected is of a known quality.

Is the activity important? (What does it get us)

< Yes, the activity is important and it gives us a picture of an industry's quality system.

Is there a product? Who is the major user of the product or information?

< Yes, there is a product (report) and OAQPS, Regions and the States will use the information.

Is this a new activity? What activity does it replace or enhance?

< No, this is not a new activity and the NPAP will provide a assessment of an industry's air monitoring network.

Brief description of current activities.

- < Most States require that the industries participate in the NPAP.
- Some PSD networks ambient air data is submitted to AIRS.

Who is responsible for the activity (currently).

< OAQPS, Regions and States are responsible for this activity.

Pros and Cons of the activity as it's currently implemented:

- Pros:! Aids State/local to evaluate the industries air monitoring networks.
  - ! Industries are requesting to participate in the NPAP.
- Cons! No mechanism in place to receive money from industry for their participation in the NPAP.
  - ! Funds being cut from the NPAP, therefore industry participation is lessen.

Ways of improving the activity:

There should be a mechanism in place to allow industry to pay for their participation in the NPAP.

Who should be providing (responsible for) this activity.

< OAQPS, Regions and the States should be responsible for this activity.

Does this require changes to the regulation or guidance?

< Yes.

Meeting Date: October 10, 2001

Agenda: Assessment/Reporting - Technical Systems Audits

Attendees: Danny France, Matt Plate, Mark Shanis, Michael Papp, Mike Miguel,

Scott Hamilton, Richard Heffern, Rayna Broadway

Quality System Element: Assessment/Reporting

Quality System Activity: **Technical Systems Audits** 

Activity Description:

Definition: a thorough, systematic on-site, qualitative review of facilities, equipment, personnel,

training, procedures, record keeping, data validation, data management, and reporting

aspects of a total measurement system

What is the function or use of this activity?

The function of the Technical System Audits (TSA) are to promote national uniformity in the evaluation of state and local agency monitoring programs and agencies performance.

Is the activity important? (What does it get us)

< Yes, the activity is important and it gives us a picture of an agencies overall performance.

Is there a product? Who is the major user of the product or information?

< Yes, there is a product and all levels of government use the TSA report.

Is this a new activity? What activity does it replace or enhance?

< No, this is not a new activity and the TSA will promote the uniformity of the air monitoring program.

Brief description of current activities.

< Most Regions and some states conduct TSA's. There may be a need to conduct TSA's of Tribal organizations.

Who is responsible for the activity (currently).

< The Regions and States are responsible for this activity.

Pros and Cons of the activity as it's currently implemented:

Pros:! Promote uniformity in the evaluation of the State/local agencies.

! TSA's can identify problem areas.

Cons! Some Regions and States are not conducting TSAs

Ways of improving the activity:

- < There should be a minimum level of tracking TSAs. (Maybe in the new AIRS)
- < Develop TSA Teams (Regions, State/local)
- < Conduct TSA of Tribal air monitoring programs.
- < Collect the various audit forms being used in the nation in one place and make available to the air monitoring community.

Who should be providing (responsible for) this activity.

< The Regions and States should be responsible for this activity.

Does this require changes to the regulation or guidance?

< No.

Meeting Date: October 3, 2001

Agenda: Assessment/Reporting - Data Quality Assessment

Attendees: Danny France, Matt Plate, Shelly Eberly, Mike Miguel, Don Gourley, Rayna

Broadway, Vic Guide, Kuenja Chung, Richard Heffern, Michael Papp,

Regina Charles

Quality System Element: Assessment/Reporting

Quality System Activity: Data Quality Assessment

Definition: the statistical evaluation of a data set to establish the extent to which it meets user-

defined application requirements (i.e., DQOs).

What is the function or use of this activity?

To ensure the quality of data collected can be used to make a decision with a desired confidence.

Is the activity important? (What does it get us)

< The activity is important. It gives us a statistical evaluation of data.

Is there a product? Who is the major user of the product or information.

< Yes, there is a product and OAQPS and the regions are the major users.

Is this a new activity? What activity does it replace or enhance?

< Yes, data quality assessments enhances the overall quality system on the nation's air monitoring program

Brief description of current activities.

< All levels of government perform data quality assessments, but not from a statistical standpoint.

Who is responsible for the activity (currently)?

< OAQPS and Regions are responsible for the activity.

Pros and Cons of the activity as it's currently implemented.

Pros:! Summary on information for criteria pollutants available in AIRS.

! Good DQOs will help develop good DQAs.

Cons:! Not many DQAs performed from a statistical standpoint.

Ways of improving the activity:

- < Provide real time feedback.
- < Provide statistical assessments (maybe available in new AIRS).
- Very composition of DQA tools Similar to the PM<sub>2.5</sub> DQO software that is being modified as a DQA tool, as DQO development on the other criteria pollutants move forward (recommendation in another section above) DQA tools will also be made available. It is anticipated that these tools would be integrated with AIRS

Who should be providing (responsible for) this activity?

< OAQPS responsibility for DQAs - The Workgroup concluded that OAQPS should be responsible for the development of DQAs for all federally required data at the reporting organization level. Assessments at the site specific level or for objectives other than federal (i.e., non-trends speciation sites) would be the responsibility of the SLTs and be described in their QAPP.</p>

Does the activity require changes to regulation or guidance?

< Yes

Meeting Date: October 3, 2001

Agenda: Assessment/Reporting - QA Reports

Attendees: Danny France, Matt Plate, Shelly Eberly, Mike Miguel, Rayna Broadway, Vic Guide,

Kuenja Chung, Richard Heffern, Michael Papp, John Gourley, Regina Charles

Quality System Element: Assessment/Reporting

Quality System Activity: **QA Reports** 

Definition: Documents describing a quality system for a particular project or program for a

particular period of time and the resultant data quality. The term is used as a catch all for various types of reports including reports on results of performance evaluations and systems audits, results of periodic data quality assessments, and significant quality

assurance problems and recommended solutions

What is the function or use of this activity?

The function of the QA Reports are to provide an overall assessment of the air monitoring program to management.

Is the activity important? (What does it get us)

< Yes, the activity is important. QA reports give us the ability to identify problem areas in our air monitoring system.

Is there a product? Who is the major user of the product or information?

< Yes, there is a product and all levels of government use the QA reports.

Is this a new activity? What activity does it replace or enhance?

< No, this not a new activity and it will enhance the quality of air monitoring data collected in the nation.

Brief description of current activities.

< Most States/locals, Regions and OAQPS use QA reports.

Who is responsible for the activity (currently)

< OAQPS, Regions and States/locals are responsible for the activity.

Pros and Cons of the activity as it's currently implemented:

Pros:! QA reports used by all levels of government.

! QA reports improves the quality system of an agency.

Cons:! PSD QA reports should be assess.

Ways of improving the activity:

< Need to assess the system audits of contractors (especially PSD).

Who should be providing (responsible for) this activity?

< Headquarters, Regions, State/locals/Tribal should be responsible for this activity.

Does this require changes to the regulation or guidance?

< Yes

Meeting Date: October 3, 2001

Agenda: Assessment/Reporting - P&A Reports

Attendees: Danny France, Matt Plate, Shelly Eberly, Mike Miguel, Rayna Broadway, Vic Guide,

Kuenja Chung, Richard Heffern, Michael Papp, John Gourley, Regina Charles

Quality System Element: Assessment/Reporting

Quality System Activity: **P&A Reports** 

Definition: Reports describing the achievement of the precision and accuracy requirements for the

Ambient Air Quality Monitoring Program.

What is the function or use of this activity?

The function of the P&A Reports are to provide an overall assessment of air monitoring data.

Is the activity important? (What does it get us)

< Yes, the activity is important. P&A reports give us the ability to identify problem areas in our air monitoring system.

Is there a product? Who is the major user of the product or information?

< Yes, there is a product and all levels of government use the P&A report.

Is this a new activity? What activity does it replace or enhance?

< No, this not a new activity and it will enhance the quality of air monitoring data collected in the nation.

Brief description of current activities.

- < Most States/locals, Regions and OAQPS use P&A reports.
- < Tribes need to use precision and accuracy reports.

Who is responsible for the activity (currently)

< OAQPS and the Regions are responsible for the activity.

Pros and Cons of the activity as it's currently implemented:

- Pros:! Summary information for precision and accuracy data is available in AIRS
  - ! P&A Reports used by all levels of government.
- Cons! PSD networks should have P&A Reports.
  - ! P&A probability limits should be reviewed.

Ways of improving the activity:

- < Correct problems of uploading precision data in AIRS.
- < Burden reduction of precision and accuracy checks should be addressed in the regulations.
- < Improve cooperation from States/locals/tribes in getting precision data into AIRS.
- < Include frequency of audits in the QAPP.

Who should be providing (responsible for) this activity?

< Headquarters, Region, State/locals should be responsible for this activity.

Does this require changes to the regulation or guidance?

< Yes

Meeting Date: October 10, 2001

Agenda: Assessment/Reporting - Quality System Audits

Attendees: Danny France, Matt Plate, Mark Shanis, Michael Papp, Mike Miguel,

Scott Hamilton, Richard Heffern, Rayna Broadway

Quality System Element: Assessment/Reporting

Quality System Activity: Quality System Audits

Definition: the qualitative assessment of a data collection operation and/or organization(s) to

establish whether the prevailing quality management structure, practices, and procedures are adequate for ensuring that the type and quality of data needed and

expected are obtained

What is the function or use of this activity?

The function of the Quality System Audit (QSA) is a process of qualitatively assessing the effectiveness of management practices in applying QA/QC to environmental data operations.

Is the activity important? (What does it get us)

< Yes, the activity is important and it gives us a picture of an agency quality system.

Is there a product? Who is the major user of the product or information?

< Yes, there is a product (report) and OAQPS, Regions and the States will use the information.

Is this a new activity? What activity does it replace or enhance?

< Yes, this is a new activity and the QAS will provide a assessment of an agency's Quality Management Plan.

Brief description of current activities.

< OAQPS and some Regions have conducted QSAs.

Who is responsible for the activity (currently).

< OAQPS, Regions and States are responsible for this activity.

Pros and Cons of the activity as it's currently implemented:

Pros:! Aids management to evaluate the entire agency's program concerning a quality system.

Cons! No joint audit form (TSA and QSA audit form).

Ways of improving the activity:

< There should be development of an audit form to include TSA and QSA.

Who should be providing (responsible for) this activity.

< OAQPS, Regions and the States should be responsible for this activity.

Does this require changes to the regulation or guidance?

< No.

# Attachment 2 QA Strategy Action Item/Recommendations Voting Results

As a result of the QA Workshop (Oct 23-25, 2001) the QA Workgroup produced a large lists of recommendations and action items for improvements to the ambient air monitoring quality system. The Workgroup compiled a list of these suggestions and voted on their priority (high-1, medium - 2, low -3), whether the improvement could be made with little or no additional resources (Y or N) and the time frame on when the recommendation should be implemented (within 1 year -1, within 2 years-2, or 3 or greater years -3). Attachment 2 provides the listing of these recommendations in order of priority (first), and time frame (second). QA Workgroup members voting on this list included State, local and Tribal monitoring agencies (12), EPA Regions (4) and EPA OAQPS (2)

	QA Strategy Action Item/Recommendations Voting Results					
Priority	Time	Recommendation/Action Item				
1.17	1.69	State and locals need to have a full time person for QA for the air monitoring programs				
1.22	1.78	OAQPS needs to develop DQOs for the NAAQS. In addition, there should be a project to evaluate converting the DQOs for PM2.5 to include performance-based standards.				
1.24	1.47	Have vendors of new instruments be required to develop adequate SOPs as part of the reference and equivalency process (may need to be added to SOP form).				
1.28	1.50	National air monitoring QA conference (annually) to help consistency (fund through 105, like AIRS conf.)				
1.31	2.00	Use of automated zero-span, precision checks to validate data				
1.35	1.18	Correct problems of uploading precision data in AIRS.				
1.39	1.81	Need DQOs to do DQA - Work on priority DQOs				
1.39	1.85	Getting DQO tool working with AIRS				
1.41	1.71	Review grant process to tie QA costs to monitoring costs				
1.41	2.03	Continue the development of Validation Templates for the other criteria pollutants				
1.44	1.90	Development of critical review criteria in AIRS				
1.47	1.76	Get more state and locals in on which documents are more important to them, in order to prioritize revisions				
1.47	1.80	Provide real time feedback.				
1.47	1.97	Redbook needs updating have calls with states and regions				
1.47	2.12	Training for TSAs, DQAs, and data validation				
1.50	1.44	QA forum for continued support and exchange of information.				
1.50	1.47	PAMS NPAP should be conducted in the January to March time frame so that potential problems can be rectified prior to the ozone season.				
1.53	1.74	Ensure grant funding is available for QA related training				
1.53	2.15	Use of the new AIRS system to develop more data assessment/validation techniques that could then be consistently used by all SLTs.				
1.56	1.33	Define or clarify attributes or responsibilities of QA person or manager				
1.56	1.72	Clear discrimination between guidance and regulation				
1.56	1.94	Training for managers so they understand components/need for QA				
1.56	2.47	Automate measurement systems as much as possible. Providing state of the art measurement, data logging/data transfer and QC systems will provide coast savings in the long run and provide for QC at higher frequency at no additional cost.				
1.59	1.63	Recommendations for NPAP program: eliminate duplication in the program, EPA could certify states that do have QA in place, conduct round robin with labs				
1.59	1.65	Need to work out details of graded approach.				
1.59	1.79	Ensure AIRS summarizes data as DQOs indicate				
1.59	1.81	Review each methods and QA for "musts" and "shalls". Identify "musts" in regulation without describing frequency or acceptability.				
1.59	2.03	Provide statistical assessments (maybe available in new AIRS)				
1.59	2.15	Combine all guidance into one document (Redbook)				
1.61	1.53	Improve cooperation from States/locals/tribes in getting precision data into AIRS.				
1.63	2.38	Use of data logging, telemetry or "lease-lines" to get data into information management systems and validation systems more quickly.				
1.64	1.69	Audit PAMS and get results out before ozone season.				
1.65	1.74	Develop audit teams from SLT and Regions in order to share experience/knowledge				
1.65	1.82	Update SRP guidance and make practical				
1.65	1.91	Develop a template QAPP (fill in the blanks) generic for any air program, not just criteria pollutants – needs to handle graded approach				
1.66	2.09	Need a mechanism to ensure corrective action from evaluation and updates in AIRS				
1.67	2.00	Development of auditing QA software tool				
1.67	2.14	Incorporate spatial representativeness (or lack thereof) into DQOs				
1.68	2.06	Streamlining audit programs (audit auditors?), SRP & NPAP				
1.69	1.85	NPEP funding through STAG is appropriate				
1.69	1.94	Develop QC checks based on system performance. Some checks, due to better, more stable equipment may not need to be checked as frequently as required or suggested.				
1.72	1.97	Burden reduction of precision and accuracy checks should be addressed in the regulations.				

QA Strategy Action Item/Recommendations Voting Results						
Priority	Time	Recommendation/Action Item				
1.75	1.60	There should be a mechanism in place to allow industry to pay for their participation in the NPAP (PSD)				
1.76	1.29	Electronic record keeping check with OEI to see if electronic files are acceptable (legally defensible?)				
1.76	1.76	Guidance to EPA regions on the need for consistency in the review of QAPPs				
1.76	1.85	Develop training on how to conduct TSA. Minimal steps to take during TSA. Include in Redbook				
1.76	2.00	Certification/accreditation program - hierarchical approach OAQPS-Regions-State/local				
1.76	2.09	Conduct TSA of Tribal air monitoring programs.				
1.76	2.21	Provide statistical assessments (maybe available in new AIRS)				
1.76	2.34	Through-the-probe zero/span/precision checks - have checks cover entire inlet/manifold systems				
1.78	1.67	Expand AMTIC Web links to training				
1.81	2.23	Use of computer technology by the site operator to access data that has been reviewed at the "central office" in order to implement corrective actions in a more real time mode				
1.88	1.71	Guidance for QAPPs should clearly state that QAPPs that are for projects covered by a QMP do not need to duplicate information in the QMP or applicable SOPs.				
1.88	1.91	Define needs for QMPs for all agencies.				
1.88	2.19	Review and develop "minimal" TSA form in Redbook				
1.89	1.97	Contractual mechanisms to provide support, such as DQO/DQA statistical support				
1.90	1.61	Less compounds could be included in the PAMS NPAP audits. Participants would prefer if higher quality standards (NIST) are utilized with less compounds.				
1.93	2.07	Develop documentation for states that opt out of NPEP				
1.93	2.25	Revise EPA QA/R-2 with the substantive changes discussed in Workshop. Will not revise R2; will create ambient air specific R2.				
1.94	1.78	Definition/interpretation of primary and transfer standards				
1.94	2.06	Can flagging help get data in sooner? Flag data in AIRS as "unvalidated" for use more real time, then pull "unvalidated" flag off quarterly or yearly				
1.97	2.14	Guidance on timeliness and consistency in performing site evaluations				
2.00	1.88	Collect the various audit forms being used in the nation in one place and make available to the air monitoring community.				
2.00	2.19	Set minimal level of conducting site evaluations (Redbook)				
2.00	2.26	Develop the guidance for small organizations and projects, such as those who can collapse the QMP and QAPP				
2.06	1.63	Look to see if there is a requirement for a central filing systems QA order 5360.1???				
2.06	2.03	Recommendations/guidance for central filing system (Redbook) including what should be in those filing systems				
2.07	1.90	Perform survey to determine "acceptable" PE programs in order to avoid redundancy.				
2.11	2.03	Place some important training in regulation				
2.11	2.06	What is reporting organization? Does this need to be re-defined or should the definition be strictly adhered				
2.11	2.33	Develop web- based training courses				
2.11	2.47	OAQPS oversight is very helpful site visits annually for some (maybe with MSR)				
2.12	2.21	Develop combo TSA, QSA audit form				
2.12	2.24	The graded approach needs to be addressed in the CFR, including specific criteria for different levels of QAPPs with examples				
2.12	2.31	Increase consistency between EPA Regional offices on how they review QMPs.				
2.13	1.57	Review Table 5-1 in Redbook- ensure agreement on record types				
2.18	1.82	Conduct polls of the Regions and State/locals on who is conducting site evaluations				
2.19	2.16	There should be a minimum level of tracking TSAs. (Maybe in the new AIRS)				
2.21	2.32	Tools to help w/DQAs, beginning with annual/3-year reports.				
2.27	1.87	Revise CFR to quarterly certifications				
2.29	2.21	APDLN - more hubs, e.g., Alaska, Guam				
2.61	2.33	Combine 58 Appendix A and B				

# Section 6. Technology

#### 6.1 Introduction

The National Monitoring Strategy seeks to provide the direction for an ambient air monitoring network that can be more responsive to current and future needs of the network. This section focuses on areas of the ambient air monitoring program that are ripe for investment in new technologies. To provide input on the areas of technology that should be considered and how they might best be implemented, an ad-hoc workgroup of SLT and EPA representatives was formed. This workgroup met in a series of teleconference calls followed by a 3 day face-to-face meeting in October 2001. Areas considered include all hardware and software used in the monitoring, calibration, logging, transfer, storage, validation, and reporting of ambient air data. Through this process, three specific areas of technology were identified as most pressing for technology investment:

- PM continuous monitoring;
- data transfer and access of ambient monitoring data; and
- tools and training that support real-time or near-real-time public reporting of data.

There are many other technology needs within the ambient air monitoring programs, such as ozone QA optimization, use of web camera technologies, and toxics monitoring. These needs should also be considered; however, each has its own special set of issues. These issues will be discussed in this section and other sections of this document. For example, ozone QA optimization is also addressed in the QA section of the Strategy.

For each of these investments to be successful, not only is a financial commitment necessary, but also a dedicated approach of eliminating barriers to technology investment. For example, in order to invest in PM continuous monitoring, there needs to be a regulatory mechanism to allow for substitution of some of the FRMs with continuous monitors. Also, there may be provisions in the current regulations and guidance that are preventing the implementation of some of these technologies. Therefore, the following recommendations are made as mechanisms to accommodate the investment of these new technologies:

- support for a hybrid network of PM monitors that provides for a substantial divestment of filter-based monitoring and investment in continuous monitoring;
- a thorough examination of ozone monitoring quality assurance that would result in recommendations leading to greater efficiency in ozone monitoring QA;
- an examination of available telemetry systems to optimize data access and transfer;

- support for investment in data management systems at the state and local agency level that could lead to more efficient processing of data; and
- accommodation for each of these areas to be included in the grant process so that available grant monies can be used for these investments.

While the recommendations above may go a long way towards fostering implementation of appropriate technology investment, the list cannot comprehensively address every need in the immediate future or longer term. SLT's, along with EPA, should continue to define areas that are best suited for technology investment.

# 6.2 Background - State of Technology in Ambient Air Monitoring

The technologies used in the ambient air monitoring program cover all hardware and software used in the measurement, calibration, logging, transfer, storage, validation, and reporting of data. Figure 6-1 illustrates the flow of data from where it is produced to where it ends up being reported. Many of the areas identified are already using state of the art technologies. For instance, much of the gaseous criteria pollutants are measured using continuous monitors with automated features for calibration and data output. However, other areas, such as data transfer, are relying on technologies that may be outdated. In some cases a technology may be somewhat antiquated; however, because it is operating smoothly and satisfying the needs of the data users, it may not be an opportune area for investment.

Figure 6.1. Data flow in Ambient Air Monitoring Systems

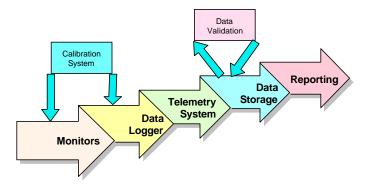


Table 6-1 breaks down an ambient air monitoring program into individual technology elements, summarizes the state of technology used in a typical ambient air monitoring program, provides initial recommendations for each technology element, and provides a qualitative assessment of the need for investment in each element.

Table 6.1. Data Flow in Ambient Air Monitoring Systems							
Technology Element	State of Technologies used in typical Ambient Monitoring Program	Recommendations	Need for new Investment				
Gaseous criteria monitoring (O3, CO, NO2, SO2)	Continuous	May need to work towards lower detection limits. See methods section	low				
Gaseous criteria calibration systems	Mixed - Everything from fully automated to manual	Move all agencies towards fully automated systems	medium				
PM monitoring	Mostly filter based	Develop hybrid network of continuous and filter based monitoring to reduce dependency on filter network and optimize resources	high - for continuous monitoring				
Data Loggers	Variety of loggers in use from ones implemented in the '80's to on-site PC's acting as data loggers	Focus on desired performance capabilities, and compatibility with calibration and telemetry systems.	medium				
Telemetry systems	Everything from low baud modems used on standard telephone lines to satellite, cable modem, DSL and other high speed internet systems.	Focus on performance needs of moving low interval data very quickly to support real time reporting and other data uses. Choose most optimal telemetry system depending on availability in area of monitoring.	high				
Data Storage	Large variety of data storage procedures from State to State; including storage on PC's, network servers, and mainframes.	No specific recommendations	medium - depends on agency. Diminishing cost of storage may be ripe for optimization				
Data Validation	Variety of validation procedures in use. Some agencies rely on complete manual validation, others use combination of automated screening and manual validation.	Work towards use of systems with automated screening.	medium - depends on agency				
Reporting	Most agencies have somewhat automated reporting systems for their continuous monitoring data.	Emphasize public reporting of data beyond ozone. Automate AQS reporting features.	medium - depends on agency				

#### **6.3** Areas of Investment

This section identifies each specific area of investment for the ambient air monitoring program. Any one air monitoring program may or may not already have invested in these areas. These areas have been identified due to either the heavy burden of already doing the work or because they are areas that data users have identified as being needed.

# **6.3.1** Monitoring

In general, continuous methods should be emphasized over manual methods. This is important for several reasons. On the resource side, continuous instruments are usually much less resource intensive to operate, provide more useful data for assessment of air quality throughout a day, have a higher sample frequency, provide for greater precision due to reduced human intervention, are easier to automate with respect to data delivery, and their data are easier to validate. On the information side, continuous data allow for real-time feedback to the public, as opposed to waiting days or weeks until filters are processed in a laboratory. The descriptions below provide the specific monitoring areas of investment being considered in this strategy.

#### **6.3.1.1 PM Continuous Methods**

A strong push for PM continuous methods is a major component of the Strategy. EPA has developed an ambitious continuous monitoring implementation plan that was borne out of requests from state and local agencies (specifically through SAMWG) and from the CASAC subcommittee on PM monitoring. Attachment 6.1 provides the continuous monitoring implementation plan, which is summarized below. Revision 2 of the plan is being developed to include recommendations of CASAC. Some of the major features of the PM continuous monitoring strategy include:

- support for a hybrid network of several hundred PM continuous monitors with a few hundred FRM samplers;
- using performance based criteria developed in the Data Quality Objective (DQO) process to determine the acceptability of PM continuous monitors in the individual networks that they are used; and
- a parallel approach for approval and applicability of methods with one option being more rigid and allowing approval of a continuous method for all monitoring objectives and a more flexible approach that allows for using these monitors for all monitoring objectives except the first order of comparison to the NAAQS.

The end goal of the PM continuous monitoring strategy is to have a PM monitoring network that can meet multiple monitoring objectives at lower cost.

## **PM Continuous Monitoring Implementation Plan Summary**

An enlarged continuous PM monitoring network will improve public data reporting and mapping, support air pollution studies more fully by providing continuous (i.e., hourly) particulate measurements, and decrease the resource requirements of operating a large network of nearly 1200 filter-based reference particulate samplers. The continuous monitoring implementation plan provides recommended directional guidance to move forward in deploying a valued continuous PM monitoring program operated by SLTs. A range of topics is addressed, including relationships between continuous and reference measurements, performance analyses of collocated continuous and filter based samplers, recommended performance criteria, regulatory modifications, and identification of outstanding technical issues and actions to be taken in the near future.

The plan proposes a hybrid network of filter based and continuous mass samplers. The hybrid network would include a reduced number of existing Federal Reference Method (FRM) samplers for direct comparison to the National Ambient Air Quality Standards (NAAQS) and continuous samplers that meet specified performance criteria related to their ability to produce sound comparisons to FRM data. Two approaches for integrating continuous mass monitors are proposed to maximize flexibility for agencies: an expanded use of Correlated Acceptable Continuous Monitors (CAC), and a new Regional Equivalent Monitor (REM) program. The CAC approach would enable agencies to address any monitoring objective, other than *direct* comparisons to NAAQS for attainment and nonattainment designations, while the REM approach would serve any monitoring objective.

In either approach, if data produced by a continuous monitor differ from that produced by the reference method, then monitoring agencies should seek to optimize the continuous method to reduce those differences. If all established means to optimize the continuous method have been exhausted, and the differences in data from the reference method and continuous monitors are still not acceptable, then the continuous data can be adjusted to be more comparable to that of the reference method. Adjustments will be allowed for the REM utilizing either raw data alone for simple regression or a combination of raw data from the instrument and physical or chemical parameters as necessary for multi-variate regression, so long as these parameters can be appropriately controlled. For instance, ambient temperature is readily available and checked on a routine schedule against a temperature standard as it directly factors into maintaining active flow control of the instrument. For a CAC, any type of adjustment will be allowed with no limitation on the parameters that can be used. At sites operating a continuous instrument that is not collocated with a reference sampler, assumptions will have to be made about the adjustment that is appropriate to produce data that is comparable to a reference sampler. The general approach proposed in the plan is to determine geographical regions representing networks of sites or a sub-set of a network; for example, rural areas and small cities, where one adjustment is appropriate for all of the continuous measurements. There is flexibility in the approval of adjustments and regions

associated with a CAC, whereas the adjustments and regions associated with the REM will be restricted and subject to an independent review through EPA's Office of Research and Development or a similar entity.

Three performance criteria are proposed to determine whether the adjusted continuous measurements are sufficiently comparable to be integrated into the PM<sub>2.5</sub> network. These criteria are bias, relative to a filter-based reference method, between -10% and +10%, measurement precision (i.e., data from two collocated continuous monitors) less than 20% coefficient of variance (CV), and an initial proposal for a correlation coefficient of 0.93 (e.g., squared correlation of 0.87) for a REM type monitor and 0.90 (e.g., squared correlation of 0.81) for a CAC type monitor. The precision and bias criteria are the result of a data quality objective (DQO) analysis that is based on data from the existing PM<sub>2.5</sub> network and an assumption that the annual PM<sub>2.5</sub> air quality standard is the principal decision driver. In a DQO analyses for the daily standard, continuous monitors, which provide what amounts to a daily sampling frequency were demonstrated to have less uncertainty around a potential decision than filter based referenced methods at lower sample frequencies, all other things being equal. Thus, the use of approved continuous monitors at sites near the daily standard should be an improvement over filter based samplers with lower sample frequencies. Also, the DQO result is conservative in that the goals estimate decision error rates for the "worst case" scenarios. In cases that are not "worst," the DQO approach allows for additional flexibility beyond the stated bias and precision goals. The correlation criteria identified provide an initial attempt to quantify a necessary minimal value for this statistic. These values were selected based on the empirical evidence of the current PM<sub>2.5</sub> continuous monitoring network and a DQO exercise to determine what observed correlation coefficient is acceptable for use with PM<sub>2.5</sub> continuous methods. These performance criteria preferably would be demonstrated by monitoring agency staff independently or in cooperation with instrument manufacturers under actual operational conditions, a departure from the very tightly controlled approach used for national equivalency demonstration. Continuous monitors would be validated periodically in recognition of changing aerosol composition and instrument performance.

#### **6.3.1.2** Ozone Methods

Although a large network of ozone monitors exists in the United States, there may be opportunities to make better use of the ozone network. This could potentially involve several specific areas of technology associated with ozone monitoring, as identified below:

- opportunities to divest of some redundant urban monitoring and relocate those
  monitors in areas outside the urban environment in order to detect the spatial
  gradient of ozone. This is expected to be largely accomplished through the
  assessments performed across regional areas.
- a comprehensive review of how ozone monitoring quality assurance is performed. This should examine the regulations as identified in 40 CFR Part 58, Appendix A

and the QA guidance in the "Red Book." A review of how state and local agencies are performing QA in their agencies should also be performed. The review should provide recommendations for areas of divestment and investment in ozone monitoring quality assurance.

# 6.3.1.3 Web Camera Technologies

Many State and local air monitoring agencies have successfully implemented web cameras to illustrate the visual quality of the air. For example, the CAMNET site (<a href="http://www.hazecam.net/">http://www.hazecam.net/</a>), implemented by NESCAUM, provides web accessible images of urban and rural scenic vistas at several sites throughout the northeast. The images have been used with air pollution data to communicate visibility and air quality. The relatively low cost of the technology combined with an effective medium for distribution of the data on state and local agency websites makes for an efficient way to communicate air quality to the public. With the growing interest in reporting and forecast ambient air quality to the public, the web cameras have become an important tool in supplementing these reports.

# **6.3.2 Information Technology**

The areas of information technology currently run in most state and local agencies may be the most ripe for new investment. This is largely due to both the need for a national network of air monitoring that can be available in real-time to support public information needs of the data, and the substantial areas of improvements that have been made in information technology since most air monitoring stations were implemented. Although commercially available information technologies may be substantially more efficient than what are currently being used by many state and local agencies, there are a number of issues to consider, such as making the best choice for investment, costs of technical support, and how easy would it be to move to another generation of this technology once the current generation is outdated. This subsection identifies some of the key issues with each area of information technology supporting an ambient air monitoring program as well as desired performance capabilities of an information transfer system to serve Level 2 and 3 NCore sites.

#### **6.3.2.1** Instrument to Datalogger

Most continuous monitors have the ability to output data at least two ways. For real-time or near real-time monitors, analog outputs usually have a DC voltage corresponding to a range of the concentrations. For example, in an ozone monitor, a 0 to 5 volt output might correspond to a 0 to 500 part per billion range. The analog output is fed into a datalogger that has been programmed to receive the DC voltage and interpret it as a concentration of ozone. A RS-232 or other output device may also be employed. These outputs can carry a substantial amount of information beyond the concentration value. For instance, operating temperature, light intensity, if applicable, and concentration range may all be carried in addition to the actual concentration. Despite the wealth of information that can be carried across an RS-232 connection, these

connections are rarely used. The primary reasons for using DC voltage outputs over RS-232 connections are the simplicity of receiving the concentration data by DC voltage and the lack of standard formats for the fields among vendors for the RS-232 connections. Despite not using these other data available via the RS-232 connection, some of the information may actually be very useful for validating data and remote troubleshooting of instruments. With the cost of storing data becoming cheaper, having an archive of these data may be an effective way to improve this component of the ambient air monitoring program. In order to move from a network where most sites are connected by DC voltage to something that provides for more information, a number of issues need to be worked through. For instance, providing the data in a common format from multiple vendors, manufacturers would allow for dataloggers to be easily adopted to receive data from any of these monitors. Also, an examination of the existing and up and coming direct connections should be made (e.g., USB, ethernet, FireWire).

## **6.3.2.2** Datalogger to Database

Once data are on the datalogger at the ambient air monitoring station, they need to be sent to servers where they can be summarized and disseminated to data users. In most cases this will occur by using a server at the office of the state or local agency. The frequency of the transfers is usually dictated by the needs of the data user. For public information use, data may need to be sent to the server every hour of even more frequently. The conventional way to get data from the monitoring stations has been to poll each of the stations individually. With more widespread availability of the internet, pushing data from monitoring sites on a regular basis will be especially effective in mapping and public reporting of data.

## 6.3.3 Reporting

The need to provide data to a number of users will require multiple reports of the information. For example, the public may need a near real-time simple message that the air is "clean" or "moderate." A health researcher or modeler may want a very detailed accounting of the available data in the shortest time intervals possible. Regulatory users generally want the data in the form that they can be compared to the NAAQS.

## **6.3.3.1 Public Reporting**

The area of public reporting for air monitoring data may provide the largest number of users of data. This area has been growing rapidly in the last few years as a result of the increased availability of air quality reporting, especially for ozone. This is expected to continue for other pollutants. Specifically, PM public reporting is expected to increase as more agencies bring their PM continuous instruments on line and EPA's AIRNOW program accepts and reports PM monitoring data.

#### **6.3.3.2** AQS Reporting

Air monitoring data is to be supplied to AQS after it has been validated at the state or local agency level. In early 2002, EPA implemented its new AQS system. The new system is expected to have a lot more functionality than the previous mainframe system. This will be especially useful to casual users of the data who were previously unable to access air monitoring data from the mainframe system.

## **6.3.4** Summary of Desired Performance for Information Transfer Systems to Support National Core Network of Ambient Air Monitoring Stations

Currently, most agencies are using the same information technology systems to record and move data from ambient monitoring stations that were implemented in the 1980's. Due to incredible improvements in processing speed and storage capacity, as well as the throughput capabilities to move data, some information technology systems currently in use may be antiquated. If one considers future needs of a national core network (NCore) of ambient air monitoring stations, such as automated low level validation and national near-real time delivery of multi-pollutant data, very few systems as currently run can meet these needs. However, in some cases systems may be adaptable to desired performance capabilities simply by upgrading the telemetry or adding additional features to existing systems. Other systems may need to be replaced entirely to meet the needs of NCore. This section summarizes the desired performance capabilities of an information transfer system to serve Level 2 and 3 NCore sites.

## **6.3.4.1** Monitoring Objectives and Performance Criteria

To define the needed performance criteria of a state-of-the-art information technology system, a matrix of needs has been developed. This matrix considers an optimal information technology system, but is not intended to address what the individual components should look like. For instance, once low-level validated data for a specific time period were ready to leave the monitoring station, a number of telemetry systems may actually accomplish moving those data. By identifying the needed performance criteria of moving data, rather than the actual system to move it, monitoring agencies may be free to identify the most optimal system for their network.

Table 6-2 summarizes each of the major monitoring objectives of NCore, the lowest monitoring interval that can reasonably achieve supporting that objective, and how quickly a national set of those data are expected to be aggregated and made available to a user community. Since an information transfer system will need to support the monitoring objectives with the tightest performance needs, the minimum design criteria are summarized at the bottom of Table 6-2.

**Table 6-2.** Monitoring Objectives and Associated Performance Needs

Monitoring Objective	Monitoring Interval Needed	Availability of Aggregated National Dataset
Public Reporting - Air Quality Index (AQI)	Hourly data	Within an hour
Mapping	5 minutes to one hour.	Within an hour
Exposure	1 minute to one hour	Within an hour
Modeling - Empirical modeling to support forecasting efforts	5 minutes to one hour	Within an hour
NAAQS	Generally 1 hour or 24 hour data are needed	Generally not needed until fully validated by monitoring agency, if lower level validated data is available as per other monitoring objectives.
Minimum Need	1 minute	Within an hour

By focusing on two of the most critical elements of an information transfer system (i.e., a minimum sample period of one minute, and moving data to be aggregated nationally within an hour), it becomes apparent that utilizing state-of-the-art telemetry systems will play a critical role in information transfer systems for NCore. Much of the other performance needs that can be identified are associated with the datalogger and associated computer. Table 6-3 summarizes some of these additional performance needs. Once again, an attempt was made to only define performance and not design criteria.

Table 6-3. National Core Network (Level II and III) Information Technology Performance Needs

Performance Need	Performance Criteria	Notes
Sample Periods	1 minute, 5 minute, and 1 hour data	1 minute to support exposure, 5 minutes to 1 hour data to support mapping and modeling. 1 hour data for Air Quality Index reporting and NAAQS.  Sample period may need to be higher for certain pollutant measurement systems depending on method sample period and measurement precision when averaging small time periods.
Data Delivery	- 15 minutes within network - 1 hour nationally	Delivery every 15 minutes of 3 sample intervals each 5 minutes a piece.  Exposure data could be supplied at 1 minute intervals for episode monitoring and as needed.
Low Level Validation	<ul> <li>Last automated zero and QC check acceptable</li> <li>Range check acceptable</li> <li>Shelter parameters acceptable</li> <li>Instrument parameters acceptable</li> </ul>	Other low level validation may be necessary
Data Availability	- all qc data, operator notes, calibrations, and pollutant data within network - Low level validated pollutant data externally	Create log of all monitoring related activities internally. Allow only validated data to leave agency network.
Types of monitoring data to disseminate - externally	- continuous and semi-continuous pollutant data - accompanying meteorological data - associated manual method supporting data (for instance FRM sample volume).	
Additional data for internal tracking	- Status of ancillary equipment such as shelter temperature, power surges, zero air system	
Relevant site information	Latitude, longitude, altitude, land use category, scale of representativeness, pictures and map of area.	Other site information may be necessary
Remote calibration	Ability to initiate automated calibrations on regular schedule or as needed.	
Reviewing calibrations	- allow for 1 minute data as part of electronic calibration log	
Initialization of manual collection methods	Need to be able to remotely initiate these or have them set at an action level from a specific monitor	

#### **6.3.4.2** Other Performance Considerations

While some of the desired performance criteria can be identified in units such as sample period or data delivery time, others are more qualitative in nature. The following list identifies some of the other important considerations of an information transfer to support NCore:

- Allow for network time synchronization of all monitoring stations;
- Have battery back-up, such as a UPS, to ensure no data loss during power outage;
- Have information transfer system be self-initializing so that if power is interrupted (even with a UPS) the system will go back on-line;
- Provide graphical display of data;
- Provide math operations of data; and
- Automate AQS processing for NAAQS data after full validation in re-engineered format.

## 6.3.4.3 Optimizing Costs of Telemetry Systems to Support NCore

Although there needs to be an initial investment in upgrading information technology systems to support NCore, there is an expectation that the added value to the program by enhancing the timeliness and frequency of data delivery will more than account for the cost. Also, since the performance criteria, presented in this section, lend themselves to utilizing state of the art telemetry systems, such as high speed internet and satellite, there will no longer be a need for leased land lines to support low speed modems.

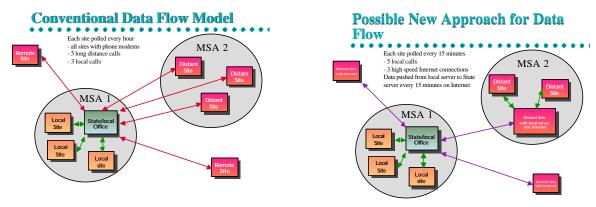


Figure 6.2 Figure 6.3

Ironically, many options for state-of-the-art telemetry systems are lower in cost than conventional systems. However, due to the cost and burden of implementing a new system, many monitoring agencies are reluctant to pursue this kind of a project. Consider the conventional data flow model in Figure 6.2 where there are five long distance calls each time the network is polled.

Now consider a possible new approach illustrated in Figure 6.3 which utilizes a combination of modems and high speed internet with no long distance calls. The savings from avoiding long distance calls can more than make up for the cost of the internet connection and local phone systems. Then the cost of frequent polling can be substantially reduced.

#### 6.4 Issues

Despite the need to invest in many areas of the ambient air monitoring program, investing blindly may never result in an improved system. Some concerns that have been brought to the attention of the Technology Workgroup, from both within the group and external to it, are identified below. As appropriate, some possible solutions to each of these issues are also presented:

- Making the right choice for a technology. For any one type of technology, there
  may be several choices to consider. The most cost-effective choice right now
  may be outdated in a year. Making the right choice needs careful consideration
  and, even then, the choice may still not be correct.
- Transition from current to new technology. Need to consider things such as downtime of systems and a contingency plan if new systems fail.
- Training of staff. New technologies may require a higher level of expertise than the old system it was replacing. Need to adequately plan for major shifts in technology.
- Technical service. Need to consider what, if any, service plan would accompany any new technology. This may affect the true cost of the technology. Also, need to consider the responsiveness of technical service.
- Use of proprietary software. Need to consider the issues regarding the use of software that is not in the public domain.
- Ability to transfer to new technologies at a future time. Agencies need to be careful to select technologies that do not prevent them from selecting a newer technology down the road.
- Identification of appropriate technical specifications to be included on purchase requests so that air monitoring agencies make the right purchase of equipment. This is especially important regarding technologies that may have similar features; however, if the lower cost product is inferior, it may lead to substantially greater problems to the end user. If purchasing agents are given an appropriate amount of detail in the technical specification, selection of the inferior technology may be avoided.

#### **6.5** Recommendations

From a technology perspective, the following summarizes the recommendations:

- support a hybrid network of PM monitors that provides for a substantial divestment of filter based monitoring and investment in continuous monitoring;
- optimize gaseous pollutant quality assurance, including automation of routine calibrations at all sites;
- clarify QA requirements when utilizing technologies for QA ptimization;
- implement state-of-the-art information technology systems that can provide data routinely in five-minute to one-hour intervals, with one-minute intervals for episodes, and be aggregated nationally within an hour;
- support investment in data management systems at the SLT level that could lead to more efficient processing of data; and
- accommodate, to the degree feasible, each of these areas to be included in the grant process so that available grant monies can be used for these investments.

## **DRAFT**

**Revision 2** 

June 21, 2002

## CONTINUOUS MONITORING IMPLEMENTATION PLAN

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Attachment A. PM<sub>2.5</sub> Continuous/FRM Analysis

Attachment B. PM<sub>2.5</sub> Data Quality Objectives

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#### List of Abbreviations and Terms

AQI Air Quality Index - An numerical and color coded index for reporting

timely air quality to the public for five major pollutants: ground-level ozone, particulate matter, carbon monoxide, sulfur dioxide, and nitrogen

dioxide.

Bias (total) The systematic or persistent distortion of a measurement process which

causes errors in one direction.

BAM Beta Attenuation Monitor - A monitor that uses a source and detector of

emitted beta particles to determine the collection of particulate matter.

CAC Correlated Acceptable Continuous (as currently applied) - A continuous

PM<sub>2.5</sub> monitor collocated with a FRM having sufficient comparability to allow for a reduction in sample frequency of the FRM from daily to 1-in-3

days.

CAMM Continuous Ambient Mass Monitor - A monitor that measures changes in

pressure drop across a filter tape with particulate matter collected on it to

determine the concentration of fine particulate.

CASAC Clean Air Science Advisory Committee - A group charged with statutorily

mandated responsibility to review and offer scientific and technical to the Administrator on the air quality criteria and regulatory documents which

form the basis for the National Ambient Air Quality Standards.

DQO Data Quality Objectives - Are qualitative and quantitative statements that

clarify study objectives, define the appropriate type of data, and specify tolerable levels of potential errors, that will be used as the basis for establishing the quality and quantity of data needed to support decisions.

FEM Federal Equivalent Method - A method for measuring the concentration of

an air pollutant in the ambient air that has been designated as an equivalent

method in accordance with 40 CFR Part 53.

FRM Federal Reference Method

Measurement

Precision (total) A measure of the mutual agreement among individual measurements of the

same property, usually under prescribed similar conditions, expressed

generally in terms of the standard deviation.

Primary Monitor Identifies one instrument as the sanctioned monitor for comparison to the

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NAAQS when there are multiple instruments measuring the same pollutant

at the same site.

REM Regional Equivalent Monitor - A potential new type of equivalent monitor

being proposed in this document that would be limited geographically in its approval to where its performance has been successfully demonstrated.

SAMWG State Air Monitoring Working Group

SES Sample Equilibration System - A technology utilizing a Naphion® dryer

that allows sample flow streams to be conditioned to low humidity and

temperature.

STAPPA/ALAPCO State and Territorial Air Pollution Program Administrators / Association of

Local Air Pollution Control Officers

TEOM Tapered Element Oscillating Microbalance - A particulate matter continuous

monitor that utilizes an inertial balance which directly measures the mass collected

on a filter by measuring the frequency changes on a tapered element.

## **Executive Summary**

An enlarged continuous PM monitoring network will improve public data reporting and mapping, support air pollution studies more fully by providing continuous (i.e., hourly) particulate measurements, and decrease the resource requirements of operating a large network of nearly 1200 filter-based reference particulate samplers. This document provides recommended directional guidance to move forward in deploying a valued continuous PM monitoring program operated by State and local agencies and tribal governments. A range of topics are addressed, including relationships between continuous and reference measurements, performance analyses of collocated continuous and filter based samplers, recommended performance criteria, regulatory modifications, and identification of outstanding technical issues and actions to be taken in the near future.

This plan proposes a hybrid network of filter based and continuous mass samplers. The hybrid network would include a reduced number of existing Federal Reference Method (FRM) samplers for direct comparison to the National Ambient Air Quality Standards (NAAQS) and continuous samplers that meet specified performance criteria related to their ability to produce sound comparisons to FRM data. Two approaches for integrating continuous mass monitors are proposed to maximize flexibility for agencies; an expanded use of Correlated Acceptable Continuous Monitors (CAC), and a new Regional Equivalent Monitor (REM) program. The CAC approach would enable agencies to address any monitoring objective, other than *direct* comparisons to NAAQS for attainment and nonattainment designations, while the REM approach would serve any monitoring objective.

In either approach, if data produced by a continuous monitor differ from that produced by the reference method, then monitoring agencies should seek to optimize the continuous method to reduce those differences. If all established means to optimize the continuous method have been exhausted, and the differences in data from the reference method and continuous monitor are still not acceptable, then the continuous data can be adjusted to be more comparable to that of the reference method. Adjustments will be allowed for the REM utilizing either raw data alone for simple regression or a combination of raw data from the instrument and physical or chemical parameters as necessary for multi-variate regression, so long as these parameters can be appropriately controlled. For instance, ambient temperature is readily available and checked on a routine schedule against a temperature standard as it directly factors into maintaining active flow control of the instrument. For a CAC, any type of adjustment will be allowed with no limitation on the parameters that can be used. At sites operating a continuous instrument that is not collocated with a reference sampler, assumptions will have to be made about the adjustment that is appropriate to produce data that is comparable to a reference sampler. The general approach proposed in this document is to determine geographical regions representing networks of sites or a sub-set of a network; for example, rural areas and small cities, where one adjustment is appropriate for all of the continuous measurements. There is flexibility in the approval of adjustments and regions associated with a CAC, whereas the adjustments and regions associated with the REM will be restricted and subject to an independent review through EPA's Office of Research and Development or a similar entity.

Three performance criteria are proposed to determine whether the adjusted continuous measurements are sufficiently comparable to be integrated into the PM<sub>2.5</sub> network. These criteria are bias (relative to a filter-based reference method) between -10% and +10%, measurement precision (data from 2 collocated continuous monitors) less than 20% coefficient of variance (CV), and a correlation coefficient of 0.93 (squared correlation of 0.87) for a REM type monitor and 0.90 (squared correlation of 0.81) for a CAC type monitor. The precision and bias criteria are the result of a data quality objective (DQO) analysis that is based on data from the existing PM<sub>2.5</sub> network and an assumption that the annual PM<sub>2.5</sub> air quality standard is the principal decision driver. In a DQO analyses for the daily standard, continuous monitors, which provide what amounts to a daily sampling frequency were demonstrated to have less uncertainty around a potential decision than filter based referenced methods at lower sample frequencies, all other things being equal. Thus, use of approved continuous monitors at sites near the daily standard should be an improvement over filter based samplers with lower sample frequencies. Also, the DQO result is conservative in that the goals estimate decision error rates for the "worst case" scenarios. In cases that are not "worst," the DQO approach allows for additional flexibility beyond the stated bias and precision goals. The correlation criteria identified provide an initial attempt to quantify a necessary minimal value for this statistic. These values were selected based on the empirical evidence of the current PM<sub>2.5</sub> continuous monitoring network and a DQO exercise to determine what observed correlation coefficient is acceptable for use with PM<sub>2.5</sub> continuous methods. These performance criteria preferably would be demonstrated by monitoring agency staff independently or in cooperation with instrument manufacturers under actual operational conditions, a departure from the very tightly controlled approach used for national equivalency demonstration. Continuous monitors would be validated periodically in recognition of changing aerosol composition and instrument performance.

A parallel effort to reduce the number of required FRM samplers nationally is under consideration. This effort may provide the divestment needed to generate operational resources to stimulate deployment of continuous mass samplers.

#### **Section 1.** Introduction

This document presents a proposal for enhancing the continuous particulate matter monitoring in the air monitoring networks operated by State and local agencies and tribal governments. The document addresses a range of topics including recommended performance requirements, regulatory modifications, and identification of outstanding technical issues and actions to be taken in the near future.

EPA is working with the Clean Air Science Advisory Committee (CASAC) technical subcommittee on particle monitoring; State and local agencies and tribal governments; and consortiums of State and local agencies on a strategy to enhance deployment and utility of continuous fine particulate mass monitors. This document is an important step in this cooperative effort as it provides a basis for comment on our intended approaches. Subsequent regulatory changes will be necessary to implement the directions in this implementation plan. Comments are welcome from all interested stakeholders on this document as well as the national air monitoring strategy it is intended to support.

The reader should be aware that the concepts and elements incorporated in this plan are singularly and collectively complex therefore creating a communications challenge. Other approaches were considered, but the potential drawbacks of a simplistic approach were not acceptable. That is, it would have been easy to develop a rigorous non-flexible program easily communicable but conveying little motivation for deployment. Similarly, a program without constraints would likely compromise data quality and interpretability. Thus, a decision was made to accommodate both flexibility and data comparability at the expense of developing and communicating a complex program.

The development of "acceptable" relationships between FRM measurements and continuous monitors is stressed throughout this document. The reason for this is that so many objectives relate to the FRM measurement (e.g., NAAQS comparisons, air quality index reporting, air quality model application). In many instances, there is no technical reason to expect comparability between disparate measurement approaches. Such comparability is desired given the utility of relating continuous measurements to a wealth of existing FRM data and to incorporate a reference marker. The downside of this approach is that the value of an FRM measurement is assumed or inferred to be greater than that of a candidate method, when in some cases the candidate method may better reflect "true" characteristics of an aerosol. This topic is addressed in more detail in Section 7.

#### **Background**

EPA is motivated to develop the continuous monitoring program by the need to improve public data reporting and mapping, support air pollution studies more fully by providing continuous (i.e., hourly) particulate measurements, and to decrease the resource requirements of operating a large network of filter-based particulate samplers. This document also addresses an important gap in technical guidance for the continuous particulate matter program, created in part by a strong emphasis to date on compliance (FRM) and chemical speciation sampling.

Approximately \$170 million has been directed toward the deployment and operation of the PM<sub>2.5</sub> network since July 1997, and the PM<sub>2.5</sub> network continues to operate at a cost of \$42 million annually. The majority of the annual expenses are for the operation and maintenance of the FRM samplers, \$26.5 million. The introduction of continuous particulate matter monitors capable of addressing multiple objectives with reduced operator burden could produce desired network efficiencies. For example, the cost of operating a FRM sampler on a 1-in-3 day schedule for a year is approximately \$19,000 (including operations, maintenance, data management, filters, and quality assurance audits). The cost of operating one of the available continuous (hourly) particulate matter samplers is approximately \$8,000. EPA does not expect that all FRM samplers will be replaced; however, significant resources can be impacted by the use of more continuous samplers in lieu of some FRM's.

Assessments of existing criteria pollutant networks are being conducted as part of a separate but parallel National Air Monitoring Strategy effort. These assessments are providing direction for reducing the current number of  $PM_{2.5}$  FRM based on observed spatial redundancy (due to relatively broad homogeneous fine aerosol behavior throughout the eastern United States) and related factors. Such divestment in filter based methods is needed to support integration of a more comprehensive continuous mass network, as well as preparing for future coarse particulate monitoring requirements. This comprehensive air monitoring strategy also has defined progress in continuously operating PM monitors as a priority for implementation.

Over the last four years, many monitoring agencies have expressed a strong desire for the development and acceptance of continuous methods for use as compliance samplers (i.e., federal equivalent methods). This sentiment has been expressed in a number of venues including the Air and Waste Management Association PM2000 Conference; through the STAPPA/ALAPCO Monitoring Committee and the Standing Air Monitoring Work Group (SAMWG); and the CASAC Technical Subcommittee on Particle Monitoring. The CASAC Technical Subcommittee on Particle Monitoring met on January 22, 2001 in a workshop session dedicated to continuous particulate matter monitoring. As a result of that workshop, EPA wrote the first draft of this implementation plan which was released in October of 2001. After presenting the concepts of this implementation plan to SAMWG and the National Monitoring Strategy Ad-hoc Technology workgroup, revision 1 of this document was released in January of 2002. On January 28, 2002, the subcommittee met to listen to presentations and comments on revision 1 of this implementation plan. As a follow up to that meeting, CASAC produced a letter report to EPA on March 1, 2002 (EPA-SAB-CASAC-COM-01-003). This version (revision 2) of the Continuous Monitoring Implementation Plan has been edited to take into account the advice of the Subcommittee, further work utilizing the DQO process and an ever-growing PM<sub>2.5</sub> continuous monitoring data set. The document provides further details on EPA's proposal to enhance continuous PM monitoring. The approach utilizes the data quality objective process to develop continuous monitor performance specifications. State and local agencies and tribal governments would have a set of parallel options through a new REM program and an modification of the existing CAC monitors provision.

The principal challenge implied within this document is maintaining an acceptable balance between data quality and technological progress. The promulgation of the 1987  $PM_{10}$  standards included a performance-based approach to the acceptance of  $PM_{10}$  methodology. The current

PM<sub>2.5</sub> monitoring network has achieved relatively high data quality due in large measure to the requirement of design-based methods (i.e., monitors with virtually identical components) and a thorough quality assurance program that followed through on a cycle of planning (data quality objectives), implementation (field/laboratory quality control), data assessment and reporting tasks. Risk in compromising data quality will emerge as an assortment of technologies are accommodated in the network. Consequently, the success of this program will rely not only on the initial data quality objective planning steps, but through a commitment to conducting the remaining quality assurance tasks and retaining the flexibility to take appropriate action in the use of data when systematic failures are encountered within the quality assurance system.

## **Document Layout**

Section 2 examines the available collocated FRM and PM<sub>2.5</sub> continuous monitoring data. This examination illustrates both the successes and challenges of implementing PM continuous monitors. Sections 3 and 4 detail the applicability of the CAC monitors and the REM including testing requirements and the approval process. Section 5 focuses on network design emphasizing the suggested hybridization of FRM and continuous particulate monitors, and proposing a new minimum number of required PM<sub>2.5</sub> FRM sites. Section 6 provides the performance standards for using PM methods and a description of the data quality objective process utilized to derive the goals for precision and bias as well as a separate but related effort for a minimum correlation coefficient. The data quality objective process recognizes a number of variables such as measurement precision, population precision, sample bias, sample frequency, a 3-year standard, and sample completeness in order to predict the confidence in a decision around an annual average and a daily standard. Section 7 addresses the use of statistical transformations for each category of continuous methods. The use of such transformations need careful consideration in terms of number of variables, frequency of adjusting, and spatial scale of applicability. Section 8 describes options for approval of methods across a spatial scale. This section details how a number of inputs such as aerosol composition using both monitored data and modeled data as well as overlaying this output with natural geographic boundaries, such as how State lines or city boundaries may be used. Section 9 provides design guidance on continuous monitoring methods. Section 10 identifies how this effort to enhance a network of continuous particulate monitors is linked to the national monitoring strategy. Section 11 provides a summary of the potential regulatory changes and schedule necessary to implement this plan. Section 12 provides a repository of issues and action items.

<sup>&</sup>lt;sup>1</sup>"CY 2000 Quality Assurance Report of the PM<sub>2.5</sub> Ambient Air Monitoring Program," U.S.EPA Office of Air Quality Planning and Standards, October 2001.

## **Applicability**

The scope and intention of this document is focused on addressing continuous particle mass monitors that provide in-situ sampling/analysis capability producing outputs that can be aggregated upward to 1-hour reporting periods (e.g., TEOM's and beta attenuation gauges). The approaches proposed rely on the use of the data quality objective process to produce quantitative performance standards. This process would in concept accommodate alternative particulate matter measurement approaches beyond the more traditional continuous mass methods, assuming performance standards are achieved. Such acceptable examples that might provide a useful alternative to the federal reference method include the use of a continuous speciation monitor alone (e.g., sulfate only) or in combination with multiple speciation monitors (e.g., carbon, nitrate, and sulfate), or other filter based methods that do not have current equivalency status (e.g., dichotomous sampler). The principles described in this document are not applicable to measurement systems beyond particulate matter (e.g., utilizing particulate matter measurements to replace ozone or other discrete gaseous measurements).

## Section 2. PM<sub>2.5</sub> Continuous/FRM Relationships

Editors note for Revision 2:

The number of PM2.5 continuous monitors reporting data to the AIRS database continues to grow rapidly. As of April 15, 2002 there were 192 PM2.5 continuous monitors registered in AIRS. 168 PM2.5 continuous monitors had data reported to the AIRS database. Initial review of these data has occurred and the same general patterns appear to be holding with regard to geographic and seasonal performance. Due to the effort necessary for analyzing a data set of this size and timing of this document, a further analysis has not been provided for in this revision. Analysis of PM2.5 continuous monitor performance are expected to be made as part separate data evaluation efforts.

#### Introduction

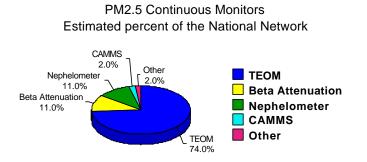
This section represents an initial effort to compile relational analyses between continuous and FRM data. Relationships between PM<sub>2.5</sub> continuous and FRM monitors are synthesized from a number of sources, including routinely collected data provided by State and local agencies and data from available field studies. The task of comparing PM<sub>2.5</sub> continuous data with FRMs was accomplished by averaging the hourly continuous mass data between midnight to midnight, to parallel the FRM operations. General information is provided first with a number of analyses presented later in this section. A more detailed set of analysis are presented in Attachment A.

## **General Summary**

Continuous monitors track FRM data with varying degrees of success across the country, with a mix of seasonal and geographical patterns affecting behavior. Analyses to date are somewhat limited by the availability of relatively few formal field studies, and the current (and temporary) situation where only one PM<sub>2.5</sub> continuous method (the TEOM<sup>2</sup> operated at 50C) has been widely deployed (Figure 2-1). Despite these limitations, there is an emerging understanding that the best PM<sub>2.5</sub> continuous monitor choice may vary from one monitoring agency to the next. TEOMs operated at 50C appear to predict FRM measurements in locations where volatile losses are minimal. Examples include sites with sulfate dominated aerosols in the Southeast (the Carolinas and Georgia) throughout the year and northeastern and upper Midwest (Iowa and Michigan) locations during the summer. The prevalence of winter month underestimates in certain areas suggests that the TEOM operated at 50 C exacerbates volatile losses during cool conditions when the difference between operational and ambient temperature is greatest. Converting the 50C TEOM to a 30C TEOM with a Sample Equilibration System (SES) should reduce cool season volatile losses. Analyses comparing collocated 50 C and 30 C TEOMs with the SES and FRMs at sites in North Carolina and New York State indicate improved comparability to the FRM for the 30 C TEOM with the SES.

<sup>&</sup>lt;sup>2</sup>Manufactured by Rupprecht & Pataschnick.

Figure 2-1 Percent of PM2.5 Continuous Methods used Nationally



The beta attenuation monitor (BAM)<sup>3</sup> is operated at several locations (second in number to the TEOM) throughout the western United States with a limited number of new locations in the east. The California Air Resources Board and other organizations sponsored a field study of several major PM<sub>2.5</sub> commercially available monitors indicating high performance of the BAM conducted during relatively volatile aerosol conditions.<sup>4</sup> EPA's Environmental Technology Verification Program (ETV) included two test sites; one in Pittsburgh, PA in the summer of 2000; and one in Fresno, CA in the winter of 2000-2001. This verification program included a number of PM<sub>2.5</sub> continuous monitors being deployed by State and local agencies including the BAM, the TEOM operated at 50C, the TEOM operated with the sample equilibration system at 30C, and the CAMMS<sup>5</sup>. While the verification reports do not offer conclusions as to the performance of the monitors, inspection of these reports indicates that the Met One BAM performed consistent at both test sites. The final verification reports from these field studies are available from the U.S. EPA web site.<sup>6</sup>

The Nephelometer is used at many sites in the Pacific Northwest. This monitor can have advantages over PM2.5 continuous methods with respect to its ease of operation. However, Nephelometers can have problems with high humidity and care should be taken to assure sample

<sup>&</sup>lt;sup>3</sup>Manufactured by Met One Instruments.

<sup>&</sup>lt;sup>4</sup>Reference the CARB report here.

<sup>&</sup>lt;sup>5</sup>Manufactured by Thermo Andersen.

<sup>&</sup>lt;sup>6</sup>Environmental Technology Verification Statements and Reports: http://www.epa.gov/etv/verifrpt.htm#07

streams are conditioned so as not to have moisture interfere with the scattering output. There are several manufacturers of Nephelometers, so care also needs to be taken when comparing data from a monitor at one site to another. Although Nephelometers do not provide for a direct output of fine particulate concentration, they can be useful when calibrated against filter based methods to provide for diurnal and day to day signal of fine particulate.

## Analysis of the Variety of Relationships for 47 Collocated PM<sub>2.5</sub> Continuous and FRM Sites

The AIRS database included 11 sites with at least a years worth of collocated  $PM_{2.5}$  continuous monitoring and FRM data based on a Spring, 2001 retrieval. An additional 36 sites were included for analyses if they had at least 3 quarters of data with at least 11 valid collocated pairs per quarter for a total of 47 sites (Figure 2-2) forming the basis for the analyses presented in this section.

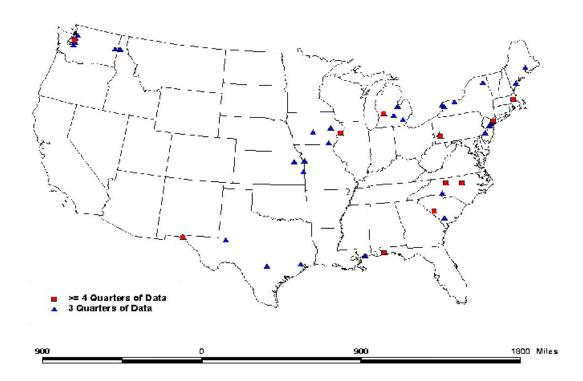


Figure 2-2 Map of 47 Sites used in PM<sub>2.5</sub> Continuous Monitors Analyses

## Intercomparisons of FRMs and PM<sub>2.5</sub> Continuous Monitoring Data:

Of the 11 sites with at least 4 quarters of complete data, 8 sites used TEOM monitors with the factory installed correction factor applied for the entire data set. This factory installed correction factor adds 3 ug to the intercept and 3% to the slope for data coming from a TEOM. A table summarizing the range of concentration values from each of the FRM and continuous

monitors at these sites is provided below:

Table 2-1 Concentration Ranges for 8 Sites with Collocated PM2.5 FRM and TEOM Monitors

250		N	Primary	Concentration Range of Data (μg/m³)							
MSA	Site ID		Monitor Type	Mean	SD	Min	Q1	Median	Q3	Max	
45037000	45037000	144	Continuous	14.50	6.42	1.37	9.85	13.46	18.88	34.75	
Aiken, SC - Augusta, GA	1		FRM	14.49	6.55	2.40	9.75	13.00	18.00	34.20	
Davenport, IA - Moline -	19163001	452	Continuous	12.00	6.49	2.92	7.26	10.53	15.30	48.81	
Rock Island, IL	5	453	FRM	12.81	7.31	2.30	7.30	11.50	16.90	46.70	
Winston - Salem, NC 370670	37067002	525	Continuous	16.23	8.05	2.66	10.29	14.45	20.95	64.02	
	2		FRM	16.89	8.70	1.60	10.60	15.00	21.70	69.70	
New York, NY 36005011 0	295	Continuous	15.40	9.26	4.69	8.85	12.85	19.24	85.38		
		FRM	15.21	9.17	3.60	8.30	12.30	20.00	53.00		
Dl. El	Pensacola, FL 12033000 4	12033000	214	Continuous	14.41	6.74	-17.7	9.90	13.02	17.94	45.83
Pensacoia, FL		214	FRM	14.03	6.89	1.00	8.60	12.70	18.41	49.30	
Pittsburgh, PA  42003006 4		Continuous	16.68	12.00	1.21	7.27	13.19	22.50	68.92		
	4	344	FRM	20.87	13.39	3.10	11.00	17.20	26.55	78.50	
Raleigh-Durham, NC 37183001	37183001	200	Continuous	15.02	6.89	2.78	10.00	13.66	18.98	45.88	
	389	FRM	15.59	7.52	3.00	10.10	14.40	20.00	52.80		

MSA Site ID	Gu ID		Primary	Concentration Range of Data (µg/m³)						
	N	Monitor Type	Mean	SD	Min	Q1	Median	Q3	Max	
53033005	033005	Continuous	13.30	6.39	3.38	9.08	11.87	15.48	44.42	
Seattle, WA	7 340	340	FRM	12.64	7.25	2.80	7.80	10.95	15.40	46.90

Inspection of Table 2-1 indicates that most of the sites appear to produce similar PM2.5 concentrations regardless of whether an FRM or TEOM is used. Only the Pittsburgh, PA site showed a large discrepancy between the mean of the FRM and PM2.5 continuous monitor. Due to this discrepancy, the Allegheny County monitoring staff were contacted to confirm the operation of the TEOM and use of default corrections factors. While the operation of the instrument was determined to be correctly identified, it was mentioned that the site is located in a community orientated location in close proximity to a large local source.

Scatter plots were produced for each of the 11 sites with at least a years worth of complete data. Data were plotted for each day where both a FRM value and a corresponding average 24-hour continuous PM<sub>2.5</sub> value were available. Separate plots for linear and log-normal concentrations were plotted for each site. The scatter plots can be separated into several categories: scatter plots with good agreement most of the time - illustrated by most points being on a straight line (Figures 2-3 through 2-6 and 2-9); scatter plots with a small but discernable amount of spread about the best fit line - as illustrated by a mild spread about the best fit line (Figures 2-7 and 2-8); scatter plots with good agreement part of the time and poor agreement in others - illustrated by a large increasing spread with concentration (Figures 2-10 and 2-11); and scatter plots that do not appear to correspond well with any pattern - illustrated by a large spread about the 1:1 relationship regardless of the concentration (Figures 2-12 and 2-13).

These first four figures represent sites in the southeastern United States where the  $PM_{2.5}$  continuous monitor appears to track the FRM reasonably well:

Figure 2-3 Raleigh-Durham, NC

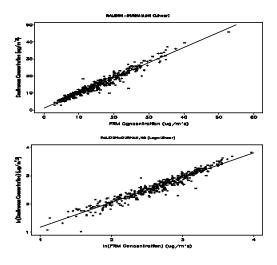


Figure 2-4 Winston-Salem, NC

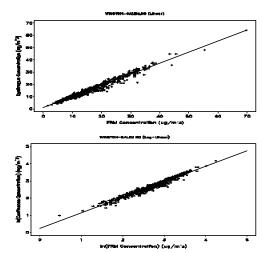
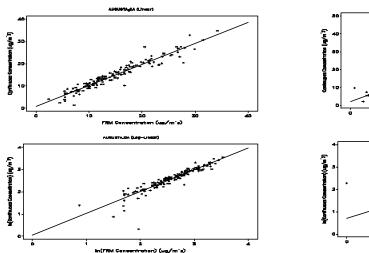
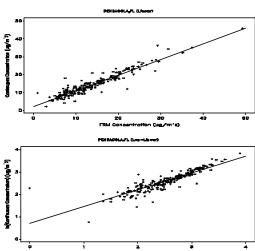


Figure 2-5 Aiken, SC - Augusta, GA

Figure 2-6 Pensacola, FL



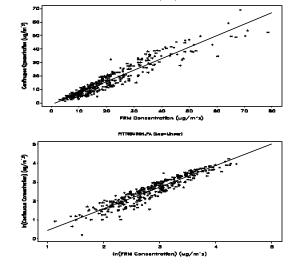


The following scatter plots represent cities in the Northeast with some discernable spread about the best fit line, but not severely distorted.

Figure 2-7 New York, NY

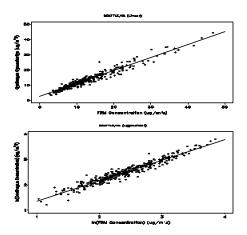
10 10 10 40 e0 PRM Canashnettan (us/m·a) NBW YBMZAY (usp-Lhear)

Figure 2-8 Pittsburgh, PA



The following figure is from a northwest site. The scatter plot shows a good fit about the best fit line.

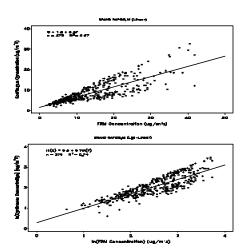
Figure 2-9 Seattle, WA



These figures, using data from sites in the upper mid-west, represent a clear spread with concentration. This is likely an effect of seasonal aerosol changes.

Figure 2-10 Davenport, IA

Figure 2-11 Grand Rapids, MI



These figures represent data from air sheds where the TEOM and FRM do appear to correspond well.

Figure 2-12 El Paso, TX

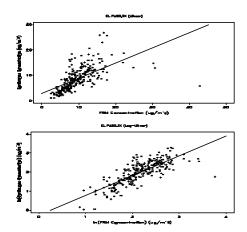
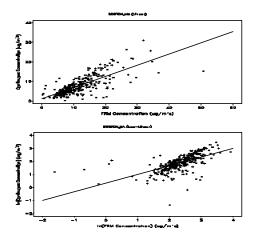


Figure 2-13 Boston, MA



### Correlation between PM<sub>2.5</sub> Continuous Monitors and FRMs

Another way to look at the data is to evaluate the goodness of fit between a model using  $PM_{2.5}$  continuous data to explain FRM measurements. The map below (Figure 2-14) illustrates the correlation coefficient ( $R^2$ ) at each of the available 47 sites. All 47 sites are able to be used because a linear model will not affect the correlation regardless of whether a site specific model is used, the standard correction factors are applied or no model is used at all. The map also indicates that geographical area plays a large role in how high a correlation coefficient is observed. This is likely due to the aerosol encountered at specific sites, the concentration of fine particulate and an effect of the season. Areas exhibiting high correlation include the Southeast, Northwest and selective locations of the Northeast. Areas with poor correlation are likely the result of either regional scale winter time volatilization as demonstrated in Iowa and Kansas or micro-scale to urban-scale influences of local sources such as in Boston and El Paso.

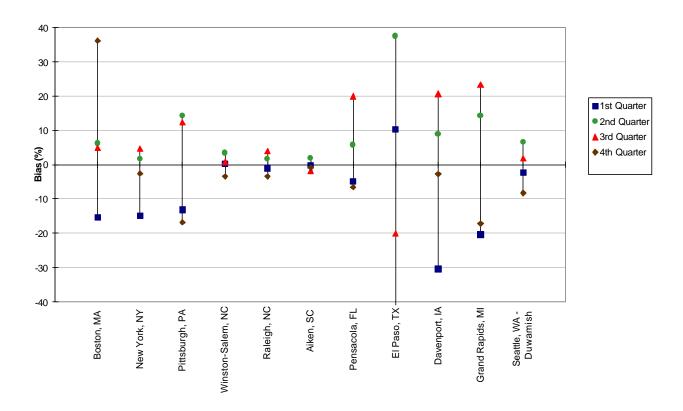
Figure 2-14 Correlation between FRMs and PM<sub>2.5</sub> Continuous Monitors



### Bias by Season

In many air sheds across the United States the species and concentration of the aerosol encountered varies by season. Changes in the species and concentration of the aerosol can lead to changes in performance of a PM<sub>2.5</sub> continuous monitor. In the illustration below the spread of bias is presented for those sites with at least 4 quarters of complete data. Bias data were calculated by comparing the FRM and collocated continuous monitoring data for days when both instruments produced a valid 24 hour value. Since some monitoring agencies choose to use a standard correction factor in the reporting of their data while others did not, each set of data was first fit to it's own linear model and then the bias were calculated by quarter. Additional graphics depicting the bias by quarter for those sites without 4 complete quarters are available in attachment 1. The tighter the fit between season the better the opportunity to use that continuous instrument to produce FRM-like measurements. Generally, cooler quarters produced the largest negative biases. This is likely due to the larger difference between the operating temperature of the TEOM and the ambient temperature of the atmosphere. The relatively high operating temperature of the TEOM during these cooler months leads to evaporation of a portion of the aerosol that are collected on a filter based sampler.

Figure 2-15 PM2.5 Bias Data for TEOM Monitors by Quarter



# Analysis of the Acceptability of the Relationship relative to the Data Quality Objective Process and Class III equivalency.

In the section above, a few of the sites appeared to have PM<sub>2.5</sub> continuous monitors that are replicating the FRM measurements very well with other sites not performing well and many sites in between. A site may be expected to replicate the FRM very well by virtue of having a scatter plot close to unity, a high correlation coefficient and a low bias. But with a variety of performances across sites, at what level should a site be considered acceptable? In this section data from 160 collocated FRM/FRM sites and 47 collocated PM<sub>2.5</sub> continuous/FRM sites are compared to various levels of the Data Quality Objective (DQO) process and the equivalency criteria. For the DQO criteria, precision and bias statistics are determined for each site and results are presented as a function of the percentage of sites that satisfied the criteria. For the equivalency criteria, linear regression is performed for each site and results are presented as a

function of the percentage of sites that satisfied the criteria.

Table 2-2 Percentage of Collocated Sites meeting individual DQO and Equivalency Criteria

Criteria	160 Collocated FRM/FRM (% of sites meeting criteria)	47 Collocated FRM/Continuous Sites (% of sites meeting criteria)
Data Quality Objective		
Bias 5%	86.9	34.0
Bias 10%	97.5	53.2
Precision 5%	28.1	0.0
Precision 10%	68.8	12.8
Precision 20%	NA	61.7
Equivalency		
Slope (1±0.05)	77.5	91.5
Intercept (±1 µg)	82.5	97.9
Correlation (\$0.97)	66.2	10.6

Interpreting Table 2-2 leads to several observations:

- Evaluations of the collocated FRM/FRM sites against the existing goals of  $\pm 10\%$  bias and  $\pm 10\%$  precision, indicate that precision is the limiting factor. Most (97.5%) of the sites meet the bias goal and 68.8 % meet the precision goal. As will be demonstrated in section 6, bias strongly influences the uncertainty of a 3 year mean, while precision has little effect due to the large number of samples in 3 years of data. Therefore, we have confidence that the FRM network is performing well, as indicted by 97.5% of the sites meeting the bias statistic.
- Evaluating the FRM/FRM sites against the existing criteria for Class III equivalency<sup>7</sup> indicates that correlation is the limiting factor with 66.2% of the sites passing. That's important since we believe we have a well-operating PM<sub>2.5</sub> FRM network; however, over one-third of the sites would fail the Class III equivalency testing criteria. If a collocated network of FRM cannot largely meet the

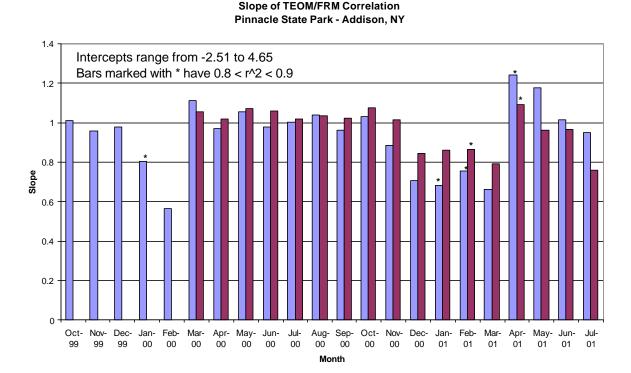
- equivalency criteria, it will be very difficult for a network of FRMs collocated with PM<sub>2.5</sub> continuous monitors to meet this criteria.
- Evaluations of the collocated FRM/continuous sites against the existing goals of ±10% bias and ±10% precision indicate that precision is also the limiting factor with 53.2 % of the sites meeting the bias goal and only 12.8 % meeting the precision goal. As mentioned above and demonstrated in section 6, bias strongly influences the uncertainty of a 3-year mean, while precision has little effect due to the large number of samples in 3 years of data. If the precision goal could be reduced to ±20%, then 61.7% of the sites in the analysis would have satisfied this criteria. Although an even less stringent precision goal could potentially be chosen, bias has now become the limiting factor for performance of the continuous monitors. While precision could potentially be relaxed and we would still have a high degree of confidence in the 3 year annual mean, the need to monitor for other monitoring objectives necessitates controlling precision to some degree. A detailed explanation of the DQO process will be explained in section 6.
- Evaluating the FRM/continuous sites against the existing criteria for Class III equivalency indicates that correlation is the limiting factor with 10.6% of the sites passing. If it can be demonstrated that the continuous monitors are producing FRM-like measurements that meet the goals established in the DQO process rather than the equivalency criteria, than the correlation criteria becomes irrelevant.

Note: In addition to this analysis the EPA has produced assessments of the quality of the PM<sub>2.5</sub> monitoring program for the currently operating FRMs for calendar year 1999 and 2000. The calendar year 1999 report is final and can be reviewed on-line at the EPA web site: <a href="http://www.epa.gov./ttn/amtic/">http://www.epa.gov./ttn/amtic/</a>. The calendar year 2000 report is in review and a draft copy can be obtained from the same web address.

#### Analysis of Collocated TEOMs with a FRM

In New York State two sites have operating collocated TEOMs with a FRM. Additionally, a site in Raleigh North Carolina also has two TEOMs and a FRM. At each site one of the TEOMs is run with an operational temperature of 50C, while the other is operated at 30C and utilizing a Sample Equilibration System (SES). Data are compared to the operating FRM at the sites, which for all 3 locations is a R&P 2025 FRM. The site with the longest record of data is located at Pinnacle State Park in Addison, NY. This site is located in a rural area of New York's Southern Tier. The illustration below provides some indication of the improvement a TEOM operated at 30 degrees C with a SES can have over operating the conventional TEOM at 50 C. The improvement is most pronounced in the cold weather months of November through March. A table summarizing regressions for all 3 sites by month is available in attachment A.

Figure 2-16 Slope of TEOM/FRM at Pinnacle State Park, NY



Data courtesy of New York State Department of Environmental Conservation and University of Albany, Albany NY.

■TM-50 ■TM-30SES

#### Conclusion

Although this analyses is very limited it's becoming clear that some areas of the country may already be operating PM continuous monitors that produce data with similar quality to that of the FRM. If a mechanism to approve the use of these continuous monitors could be made where the performance of the instrument is defined to be acceptable than a large resource savings may be gained by divesting of some of the FRM operations. Other areas of the country may not be producing PM2.5 continuous data that could be used to replace the FRM. For these areas, agencies may need to pursue improvements to their instrumentation or new technologies altogether. Comparing the performance of sites that have a collocated FRM/FRM pair with a collocated FRM/continuous pair to the expected equivalency criteria revels that the correlation statistic (R \$0.97) would be the limiting factor for either FRMs or continuous monitors to meet equivalency. Section 6 of this document examines the performance standards of PM2.5 continuous monitors in detail.

## Section 3. Enhanced Correlated Acceptable Continuous Methods (CAC)

Enhancements to the existing provisions for CAC monitors are being proposed in concert with a new REM program to provide agencies with options to enhance their network of PM continuous monitors. Rationale based on data comparability for selecting the CAC or REM vehicle is discussed in Sections 5 and 6. The basic premise of a revised CAC is to provide flexibility in method selection for PM monitoring sites that are not needed for direct comparison to the NAAQS and for sample frequency relief. These sites would be allowed to use CAC monitors if they meet specified performance criteria. While the current provisions for CAC(s) only allow for a reduction in sample frequency of the accompanying FRM/FEM, the provision under consideration would also allow for a continuous monitor to be approved for use without the collocation of a FRM at sites that are not required for the NAAQS. This additional flexibility is being considered for CAC monitors since agencies are not utilizing the currently defined CAC and it would be better to enhance the usefulness of CACs rather than to have another provision in the regulation. This approach would potentially be targeted for those agencies that need to monitor for a number of monitoring objectives other than NAAQS attainment decisions. Thus, while the CAC that is not collocated with an FRM cannot be used for attainment decisions, it can be used to meet all other applicable monitoring objectives, such as: public reporting, trends, mapping, and exposure. By allowing a portion of the currently required FRM sites in a network to be substituted with continuous monitors meeting performance based criteria, the monitoring agencies can realize a reduction in resource requirements while maintaining data delivery with an acceptable defined level of quality. Also, some of the remaining FRM sites would be collocated with the same continuous methods as the CAC's to provide the performance data for ongoing assessment of the continuous method. These revised CAC's would be different than the conventional FEM's in that they could only replace a limited number of sites and the CAC met the performance criteria specified in Section 6 - Performance Standards for Continuous Monitoring. CAC's would be different from REM's in that they could not be used for direct attainment decisions unless collocated with a FRM and meeting the performance criteria identified in Section 6. Also, there would be much more flexibility in the use of data transformations as described in Section 7 - Data Transformation Policy and Guidance. This section describes the current provisions for CAC monitors and lays out the potential scope of using CAC's in a revised network.

#### **Performance Criteria**

There are two sets of performance criteria to consider. The first set of criteria are the performance standards for acceptance of a method including individual criteria for bias, measurement precision and correlation. These criteria are provided for in section 6 with bias and measurement precision based upon the goals for measurement uncertainty as developed in the data quality objective process for the PM<sub>2.5</sub> monitoring program. A correlation coefficient is also included and is based on a DQO type exercise and an evaluation of the current network. Since the CAC is not used for regulatory decision making, the specific criteria for precision, bias and correlation at a site or network of sites will remain "goals" and not requirements. The second type of criteria are for on-going evaluation that the method is providing data of sufficient quality for its intended monitoring objective. These criteria are the same performance standards developed for measurement uncertainty in the PM<sub>2.5</sub> monitoring program and are also presented in Section 6 of

this document.

## **Testing Requirements**

There are a number of testing requirements that need to be considered. These testing requirements are intended to be designed so that State and local agencies can readily implement a field testing program to pursue a CAC for use in their network. The table below identifies the suggested criteria and rationale for CAC's:

Table 3-1 Test Specification for PM<sub>2.5</sub> CAC's

Testing Requirement	Suggested Criteria for CACs	Rational for Criteria	
Number of Test Sites	1 on a site by site basis or minimum of 2 for a network (see Table 3-2 below)	Need to demonstrate that the method can meet performance criteria at a specific site or multiple locations in a State or local network.	
Number of FRMs per site for generating baseline data in testing	1 - However strongly suggest locating test sites at collocated FRM precision sites to assure control of FRMs and to have high sample completeness	Precision of FRM can be assumed from FRM network precision statistic	
Number of Candidate Samplers	Encourage 2 for first CAC site, 1 each for each additional site tested.	Need to have collocated candidate CACs in order to calculate measurement precision of the continuous method for at least one site in the network.	
Number of hours to make a valid 24 hour sample for comparison to the FRM	18	75% completeness of the 24 hour period	
Length of testing	All 4 seasons - however testing can begin and end at any point during the year	Need to assure that changes in aerosol or meteorology related to changes in season can meet performance requirements.	
Number of data pairs - Primary Monitors, both the FRMs and the candidate CACs	90 per site with at least 20 per season See reference in section 7	Expected to be similar to 1 in 3 day sample frequency at 75% completeness for four seasons	
Number of data pairs - Collocated FRMs	As found in network	Use existing collocated FRM precision sites	
Number of data pairs - Collocated candidate CACs	- 60 sample pairs - At least 15 sample pairs per season	Based upon 90% confidence that the precision statistic is within 15% of the true precision. Since these are continuous methods may expect to have a substantially large data set.	

Range of concentrations for siting	As found in the area of consideration.	Need to evaluate method under the conditions in which it will operate.
Range of concentrations for use in data set when determining performance of methods	May (but not required to ) exclude values where the FRM concentration is below 6 ug/m³. Exclusion of values due to low concentrations does not result in failure of completeness requirements	As concentration values approach 0, biases can appear large. By focusing on the values that are above 6 ug/m³ estimates of the performance of the candidate methods are more stable.

## **Guidance for Developing Boundaries for Applicability of CAC**

Section 8 of this document provides the detail for how the appropriate geographic size is determined for use of an approved CAC.

## **Number of test sites for Collocated Acceptable Continuous monitors**

The number of test sites for CAC's depends on a number of factors such as whether one site or a network of sites is being considered for approval of a CAC and the homogeneity of the aerosol across the area of consideration. At a minimum, two sites are to be tested to support a candidate CAC across a network. The following table details how many sites are to be tested, assuming the aerosol is homogeneous across an area in which it is being tested:

Table 3-2 Test Site Specifications for PM<sub>2.5</sub> CAC's

Geographical Area of Consideration for CAC	Number of Test Sites
One MSA	2
Multiple MSA's in the same air district or State	1 for each MSA up to the first 3 MSAs, plus at least 1 site in a rural county.
Multiple States	1 for each MSA up to the first 2 MSAs, plus at least 1 site in a rural county. For each additional State add 1 urban and 1 rural site.

Note: If the aerosol is expected to vary according to the guidance provided for in section 8, then apply test sites as if each State or air district were performing testing separately. This will ensure that for each type of aerosol encountered a minimum number of sites are tested.

#### **Review Procedures**

Since the monitoring objectives for CAC's do not include direct comparison to the NAAQS, the approval procedures for use of a method should be streamlined. Thus, the review procedures should be included in the annual network review that is submitted by the State, local, or Tribal Agencies to the Region. The Region would work to determine that the performance criteria have been appropriately addressed and the continuous method is suitable for inclusion in the network. Since many agencies potentially seeking the CAC approach for relief from FRM sampling are expected to be substantially below that standard, the Regions should work towards approval of the CAC's where they make sense and not prevent their approval if a specific goal is not met. For instance, one way for Regions to make a good decision on the approval of a CAC is to utilize the DQO tool that has been developed with inputs of a number of variables and see if the uncertainty around the NAAQS would be worse or better. If the goals for measurement uncertainty are  $\pm$  10% bias and 20% CV and the agency has a bias of 5% and CV of 23% with their continuous method, then the uncertainty around the NAAQS may actually be better.

## **Ongoing Evaluation of Method Performance**

Since the CAC is not to be used for direct comparison to the NAAQS, the specific QA/QC requirements of the PM<sub>2.5</sub> quality system do not apply in a strict sense. However, since the data are to be used for a number of other important monitoring objectives the PM<sub>2.5</sub> quality system does apply in a qualitative sense. This means that agencies must develop appropriate measures to determine precision and bias estimates for the CAC monitors used in their network, but they are not held to specific numbers as if they were regulatory monitors. Additionally, the CAC's should be appropriately addressed in the monitoring agencies Quality Assurance Project Plan (QAPP). Agencies should be evaluating the quality of their network on an ongoing basis and work to resolve problems as they are encountered.

### Potential Use of CAC's in PM<sub>2.5</sub> Monitoring Networks

The expected outcome of having a CAC approved for use at a site or in a monitoring network is that it can be used in combination with a limited number of FRM's as part of a "hybrid" network. Section 5 of this document lays out the detailed network design of a potentially revised network.

#### **Section 4. Regional Equivalent Monitors**

A provision to allow for REM's is proposed to enhance the network of PM continuous monitors. The basic premise of a REM is that when a PM<sub>2.5</sub> continuous method meets the performance criteria identified in Section 6 and the testing specification described below for one or more sites in a network, then this method may be used at that single site or any sites in the network covered by the range of conditions tested. The spatial extent of the approval of the method would be based upon a number of factors such as number and location of sites tested, homogeneity of the aerosol in the network, and local contribution of the aerosol. This flexibility is being considered since some methods are expected to work well in replicating FRM measurements across specific agencies networks across all seasons, but not in every network in the country. Approved REM's would be allowed to be used for attainment decisions as part of a "hybrid" network of PM<sub>2.5</sub> FRM's and continuous monitors as described in section 5 - Network Design. For implementation purposes, REM's are different than the conventional FEM's in that they are only for use in a specific network or a subset of a network and a minimum ratio of FRM's must be retained across the network. Site REMs are used with model development on a site by site basis and have the potential to be implemented quickly. Network REMs are approved across a series of sites with the method, including statistically developed models, if necessary, consistently implemented. During the testing phase of a candidate REM, the FRM is identified as the *Primary* monitor, meaning it is the monitor to be used for comparison to the NAAQS at that site. If a continuous monitor is approved, this new REM now becomes the primary monitor with the FRM becoming a QA monitor. The REM's are different from CAC monitors in that data from REM's are used for direct comparison to the NAAQS, while data from CAC's are not. Since the data from REM's are used for comparison to the NAAOS, there is much more control on the approaches for data transformations, as described in Section 7. This section describes both the site and network REM as well as the test specifications and approval process.

#### Site REM

A provision for a site specific REM is being added so that monitoring agencies can potentially reduce sample frequency at required daily or 1 in 3 day sites to a 1 in 6 sample frequency regardless of the concentration at the site. This has the potential for an expedited implementation since the FRM data would still be available if the continuous monitor did not satisfy the performance criteria identified in section 6. If necessary, a model, as identified in section 7 would be used based upon the historical data from the site. If the correlation coefficient is satisfied between the FRM and continuous monitoring data, the sample frequency of the FRM can be reduced. The bias criteria for the historical data need not be met since the model would potentially account for the differences between the two methods. The model would be used as part of the approved continuous monitors method. The continuous monitor now becomes the approved primary monitor for the site. Each year the continuos monitoring data would be evaluated and if necessary, a new model would be developed. New models would only be used in a prospective mode. If the uncertainty of the PM2.5 continuous monitoring data is determined to be unacceptable as determined from the DQO software tool or similar approved analyses, then the continuos monitoring data is to be invalidated and the FRM data is used for comparison to the NAAQS. Since a provision already exists for "Approval of non-designated PM2.5 methods at specific

individual sites" (40 CFR Part 58, Appendix C, section 2.4) the site REMs has the potential for quicker implementation than other proposals in this document.

#### **Network REM**

Network REMs can be used at any site in a network where the performance criteria as identified in section 6 are met. Network REMs can be limited to a range of sites if testing demonstrates the performance criteria are satisfied for some grouping of sites but not others. The method for a network REM is to be consistently deployed with only one transformation used, if necessary. Thirty percent of the network REM sites are to be collocated with FRMs for ongoing evaluation of the continuous monitoring data consistency with the historical record. Once the REM is approved, the FRM sample frequency can be reduced to 1 in 6. At this point the approved REM becomes the primary monitor and the FRM becomes the QA monitor.

#### **Performance Criteria**

There are two sets of performance criteria to consider. The first set of criteria are the performance standards for acceptance of a method including individual criteria for bias, measurement precision and correlation. These criteria are provided for in section 6 with bias and measurement precision based upon the goals for measurement uncertainty as developed in the data quality objective process for the  $PM_{2.5}$  monitoring program. A correlation coefficient is also included and is based on a DQO type exercise and an evaluation of the current network. The second type of criteria are for on-going evaluation that the method is providing data of sufficient quality for its intended monitoring objective. These criteria are the same performance standards developed for measurement uncertainty in the  $PM_{2.5}$  monitoring program and are also presented in Section 6 of this document.

#### **Testing Requirements**

There are a number of testing requirements that need to be considered. These testing requirements are intended to be designed so that State and local agencies can readily implement a field testing program to pursue a REM for use in their network. Monitoring agencies may collaborate with other parties including instrument manufacturers in the testing process; however, the agency seeking approval of a REM is responsible for overseeing the field testing as if it were part of their routine operation. This will demonstrate operation of the instruments under typical field conditions as if they were already approved. The table below identifies the required criteria and rationale for REM's:

Table 4-1 Test Specification for  $PM_{2.5}$  REM's

Testing Requirement	Suggested Criteria for REMs	Rational for Criteria
Number of Test Sites	One for site REM or minimum of 2 for network REM (see Table 4-2 below)	Need to demonstrate that the method can meet performance criteria at individual site or multiple locations in a State or local agency network.
Number of FRMs per site for generating baseline data in testing	1- However strongly suggest locating test sites at collocated FRM precision sites to assure control of FRMs and to have high sample completeness	Precision of FRM can be assumed from FRM network precision statistic
Number of Candidate Samplers	1 for a site REM or 2 for first network REM test site, 1 for each additional site	Need to have collocated candidate REMs in order to calculate measurement precision of the continuous method for at least one site in the network.
Number of hours to make a valid 24 hour sample for comparison to the FRM	18 - valid hourly values within the midnight to midnight period.	75% completeness of the 24 hour period.
Length of testing	All 4 seasons - however testing can begin and end at any point during the year.	Need to assure that changes in aerosol or meteorology related to changes in season can meet performance requirements.
Number of data pairs - Primary Monitors, both the FRMs and the candidate REM	90 per site with at least 20 per season. See reference in section 7	Expected to be similar to 1 in 3 day sample frequency at 75% completeness for four seasons
Number of data pairs - Collocated FRMs	As found in network	Use existing collocated FRM precision sites
Number of data pairs - Collocated candidate REMs	- 60 sample pairs for the REM - At least 15 per season for the REM.	Based upon 90% confidence that the precision statistic is within 15% of the true precision. Since these are continuous methods may expect to have a substantially large data set.
Range of concentrations for siting	As found in the area of consideration.	Need to evaluate method under the conditions in which it will operate.

Range of concentrations for use in data set when determining performance of methods	May (but not required to ) exclude values where the FRM concentration is below 6 ug/m³. Exclusion of values due to low concentrations does not result in failure of completeness requirements	As concentration values approach 0, biases can appear large. By focusing on the values that are above 6 ug/m³ estimates of the performance of the candidate methods are more stable.
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# Guidance for Developing Boundaries for Applicability of Regional Equivalent Monitors

Section 8 of this document provides the detail for how the appropriate geographic size is determined for use of an approved REM.

# **Number of Test Sites for Regional Equivalent Monitors**

The number of test sites for REM's depends on a number of factors such as the area of consideration for approval of a REM and the homogeneity of the aerosol across the area of consideration. At a minimum, two sites are to be tested to support a candidate REM. The following table details how many sites are to be tested assuming the aerosol is homogeneous across an area in which it is being tested:

Table 4-2 Test Site Specification for PM<sub>2.5</sub> REM's

Example Geographical Area of Consideration for REM <sup>8</sup>	Number of Test Sites
Site REM	1
Network REM - One MSA	2
Network REM - Multiple MSA's in the same air district or State	1 for each MSA up to the first 3 MSAs, plus at least 1 site in a rural county.
Network REM - Multiple States	1 for each MSA up to the first 2 MSAs, plus at least 1 site in a rural county. For each additional State add 1 urban and 1 rural site.

Note: If the aerosol is expected to vary according to the guidance provided for in Section 8, then apply test sites as if each State or air district were performing testing separately. This will ensure that for each type of aerosol encountered a minimum number of sites are tested.

<sup>&</sup>lt;sup>8</sup> The example presented at best reflects a minimum requirement. Definition of extent of regional applicability is addressed more completely in section 8 and is a topic requiring significant development.

#### **Review Procedures**

The approval of a "Regionally" equivalent monitor should follow the same process for review and approval of other federal equivalent methods. This process works through the Office of Research and Developments National Exposure Research Laboratory (NERL) Reference and Equivalency program. That program receives, reviews, and provides feedback to vendors and other parties that have applied for equivalency. Once all the criteria have been appropriately addressed and the candidate method has been determined to meet the appropriate performance criteria, the Reference and Equivalency program makes a recommendation that the method be approved as "equivalent." Once approved by EPA as "equivalent," a notice is published in the Federal Register indicating that this status has been achieved. Any geographic limitations to a methods approval would also be included in this notice.

# **Ongoing Evaluation of Method Performance**

Since the REM is to be used for NAAQS decision making, all applicable elements of the PM<sub>2.5</sub> quality system are to be applied to its use. This means that REM's are to be collocated with both FRM and the same continuous method as the primary monitor as well as being subject to performance evaluation audits defined in Appendix A of Part 58. Additionally, the CAC's should be appropriately addressed in the monitoring agencies QAPP. If for 3 consecutive years the REM does not meet the DQO's and a examination of the data indicates that the uncertainty in decision errors is increasing, then the monitoring agency should - **NOT SURE WHAT THE CONSEQUENCE SHOULD BE.** Would like to have agencies work through a solution.

# Potential Use of Regional Equivalent Monitors in PM<sub>2.5</sub> Monitoring Networks

The expected outcome of having an REM approved for use in a monitoring network is that it can be used in combination with a limited number of FRM's as part of a "hybrid" network. Section 5 of this document lays out the detailed network design of the a potentially revised network.

#### **Section 5 - Network Design**

#### **Introduction:**

The PM<sub>2.5</sub> monitoring program has been implemented with a heavy emphasis on FRM samplers in order to support comparing mass data to the NAAQS. Approximately 1,143 (July 11, 2001 AIRS) monitoring sites in the United States are now operational with FRM samplers. The entire PM<sub>2.5</sub> network includes components for chemical speciation and advanced measurements (Attachment B). Only the FRM or FEM can be used for direct comparisons to the NAAQS. This plan proposes a more balanced hybrid network of filter based and continuous mass samplers. assuming that data analysts would incorporate filter based and continuous methods (seamlessly) when utilizing network data for broad scale spatial applications such as positive matrix factorization (PMF) and air quality model evaluation. This hybrid network would include a reduced number of existing FRM samplers for direct comparison to the NAAQS and continuous samplers that meet specified performance goals related to their ability to produce sound comparisons<sup>9</sup> to FRM data. Two approaches described in Sections 3 and 4 for integrating continuous mass monitors are proposed to maximize flexibility for agencies; an expanded use of CAC Monitors and REM'). The CAC approach would enable agencies to address any monitoring objective, other than *direct*<sup>10</sup> comparisons to NAAQS for attainment and non-attainment designations, while the REM approach would serve any objective.

There is an unknown amount of degraded data quality risk associated with moving from the current design based system to one relying on performance based specifications. Therefore, this hybrid network will maintain a core of FRM's to maintain an ability to quantify the relationship between FRM's and continuous samplers for continuity to both the historical record as well as ongoing and prospective use of continuous methods. The remaining network of FRM's might constitute 30% to 50% of the current network. A large network of continuous monitors meeting performance criteria would eventually be in place to improve the data base for: public reporting of Air Quality Indices (AQI) and mapping through AIRNow; supporting health effects and exposure studies addressing short-term exposures; evaluating air quality models and emission inventories, and supporting compliance needs related to direct comparisons with the NAAQS and delineating the spatial extent of attainment/nonattainment areas.

<sup>&</sup>lt;sup>9</sup> Comparability between FRMs and continuous samplers is desired, based on the extensive FRM network available. This practical need also recognizes inherent differences between measurement principles of integrated and continuous methods and does not assume any one type of measurement best represents true atmospheric aerosols conditions. Further discussion on incommensurabilities between measurement systems is provided in section 7.

 $<sup>^{10}</sup>$  Data from CACs would be expected to be incorporated in as yet undetermined weight-of-evidence analyses to define boundaries of non-attainment/attainment areas.

# **Minimum Number of FRM Samplers**

A separate but parallel effort is underway to better identify redundant monitoring for all pollutants as part of the National Monitoring Strategy (see Section 10). This national strategy supports an investment in continuous PM monitors balanced by a divestment in PM<sub>2.5</sub> FRM sampling. Progress in enhancing PM continuous monitoring requires a burden reduction in FRM sampling. Currently, nearly 1,100 FRM samplers operate across the United States, and an additional 200-300 IMPROVE and continuous samplers. The spatial richness this network should not be severely compromised; however, areas of redundancy are evident based on a variety of national and regional based assessments that illustrate broad expanse of homogeneous aerosol behavior. A reduction in required FRM samplers is possible using network assessment processes to determine effective numbers of samplers across regional and urban spatial scales. Nationally, we are suggesting that a minimum of 300-500 FRM/FEM's be retained to ensure consistency with the existing network, and provide the primary regulatory base of data. A total of approximately 600 equivalent samplers (including FRM's, FEM's and REM's) for direct comparisons to the NAAQS are recommended. The network size of approximately 600 is based on several data analyses. One analysis shows that the large spatial patterns in PM<sub>2.5</sub> are nearly identical whether using 300 or 1,200 monitoring locations in an area that covers much of the eastern United States. A second analysis indicates that several urban areas are likely over-sampled by approximately 25-35%. Perhaps as many as 1,000 (or more) PM<sub>2.5</sub> mass (FRM and continuous) sites nationally are needed for spatial characterization, but request that actual number of sites be a function State/local agency discretion as agencies must balance several competing monitoring priorities. Note, that this approach while increasing flexibility could have unintended negative consequences by accommodating too many diverse methods that do not relate well with each other. Agencies are encouraged to strive for consistency in deploying their continuous PM network and consider not only consistency of methods within an agency, but attempt to harmonize technology across regional areas.

Table 5-1 summarizes the applicability of each monitoring method category to the type of site in the network. Tables 5-2 and 5-3 include examples of revised network requirements for  $PM_{2.5}$  samplers. Specific modifications to the  $PM_{2.5}$  monitoring regulations are being addressed through a workgroup of State/local agency, Tribal nation, and EPA representatives (see section 11).

Table 5-1 PM Method Applicability

		Required Sites for NAAQS					
Method	< 80% of NAAQS	80% to 120% of NAAQS	>120% of NAAQS	Sites that are currently required but are not required in a future network.	Current Supplemental Sites	Background and Transport Sites	Speciation and IMPROVE
FRM/FEM	Т	Т	Т	Т	Т	Т	
Site REM	T • With collocated FRM operating 1-6	T • With collocated FRM operating 1-6	T • With collocated FRM operating 1-6	Т	Т	Т	
Network REM	T • With 30% FRM collocation in network	T • With 30% FRM collocation in network	T • With 30% FRM collocation in network	Т	Т	Т	
CAC	T • With 100% FRM Collocation in network FRM operates 1-6		T • With 100% FRM Collocation in network FRM operates 1-6	Т	Т	Т•	
IMPROVE						Т	Т
Speciation						т•	Т
Existing Continuous mass PM					Т		

The method category in the row is applicable for the monitoring objective in the column.

<sup>•</sup> This symbol indicates a change to the monitoring regulation is needed

# **Method Applicability Summary**

FRM/FEM/REM - These methods can be used at a required site, regardless of the concentration; at any current or future supplemental sites; and at any background or transport sites. REM's have two categories:

- 1.) Site REM's have an approved continuous monitor collocated with a FRM. Once approved the continuous monitoring data is used for comparison to the NAAQS. If the uncertainty of the continuous monitoring data is outside of the goals for the PM2.5 monitoring program (utilizing the DQO software or similar approved analyses) and worse than that of the FRM, the continuous monitoring data is to be invalidated and the FRM data shall be used for comparison to the standard.
- 2.) Network REM's have at least 30% collocation with FRM's when they are sited at required sites. Once approved the REM would be the primary sampler when collocated with a FRM.

CAC - This monitor could provide relief up to three new ways:

To convert a site from a filter based sampler to a CAC:

- 1.) At current supplemental, background, and transport sites CAC monitors may be used as the primary monitor. Collocation at these sites would follow the provisions of Appendix A; which is expected to be 15% collocation with the first collocated monitor being an FRM and the next one being of the same make and model as the CAC.
- 2.) The minimum number of required sites is to be reduced in Appendix D of Part 58. There is an expectation that there will be more sites operating than the minimum number required. For sites that are no longer required to be operated; but the agency still intends to operate the site to meet other monitoring objectives, the agency may choose to operate the site with a CAC. Appendix A collocation requirements would apply for these CAC's. Moreover, it is feasible that revised monitoring regulations may require a similar total number of monitors currently required or operating (i.e., 850 to 1,100) with a subset required to have reference/equivalent status and the remainder being satisfied by an equivalent/reference or CAC designation.

To provide additional sample frequency relief:

3.) For required reference/equivalent sites (current or future) that are either substantially above or below the NAAQS, the CAC may be operated to provide a signal of PM provided it is collocated with a FRM operating on at least a 1-in-6 day schedule. The FRM maintains the status as the primary monitor.

The conventional sample frequency relief for a CAC would still apply:

A FRM site that is required to operate daily may have its sample frequency reduced to 1-in-3 provided it is collocated with a CAC regardless of the concentration or NAAQS status.

Network Design Criteria for PM<sub>2.5</sub> Required SLAMS **Table 5-2** 

Network Design Criteria	Current Network	Example Revised Network
Required minimum number of sites at State and local Air Monitoring Stations (SLAMS)	* 100 are for background and can use IMPROVE samplers	Assuming ~600 sites are reasonable we envision a hybrid network of FRM and continuous methods meeting acceptable performance standards. A minimum of ~ 30% of each monitoring agencies future network would be required to remain as FRMs.
Scale of representativeness - Annual Average	Neighborhood or Urban Scale with FRM or FEM	Neighborhood or Urban Scale with FRM/FEM or hybrid network of FRM and continuous monitors meeting performance based criteria
Scale of representativeness - Daily Average	Micro, Neighborhood, Urban Scale	Micro, Neighborhood, Urban Scale. For sites that are expected to only have a violation of the daily standard, but not the annual average, site with a FRM/FEM. Collocated with a Continuous monitor, if needed

#### **Section 6 - Performance Standards for Continuous Monitoring**

#### Introduction

The current expectations for  $PM_{2.5}$  continuous monitors to receive federal equivalent monitor designation require field testing at multiple locations covering a range of environmental and aerosol conditions, over an entire year. The field data must meet conservative performance specifications that include slope, intercept, correlation and a precision test. If a candidate method meets all the criteria at each test site, then it receives an "equivalency" designation for use anywhere in the national network. The assumption is that the method will perform as intended in all areas if it meets these strict performance specifications at the test locations. Also, once a method receives an equivalency designation, no additional field tests are required to ensure that the equivalency holds through time.

The approach presented in this section attempts to link the testing requirements and the ongoing performance requirements to the Data Quality Objectives (DQOs). The DQOs identify the level of uncertainty in the data that is acceptable, given the intended use of the data. Methods that meet or are of better quality than identified in the DQOs can be used in the networks in which they were tested, provided they continue to meet the DQOs through time. The PM<sub>2.5</sub> Data Quality Objectives were developed for comparison of values around the 3-year annual average NAAQS since it was found to be the controlling standard (i.e. any violation of the daily standard would in almost all cases be in violation of the annual standard). However, if the daily standard is lowered it may be as influential as the annual standard in some areas. Therefore, this section will also provide information on the daily standard.

An additional DQO exercise has been performed to determine a minimum correlation coefficient for each category of continuous monitor being proposed. Since correlation was not factored into the DQO design for the PM2.5 monitoring program, it was not clear how to integrate correlation in these DQOs. The development of the correlation DQOs rely on testing whether a "true" correlation is at or below a certain value for each category of continuous monitors. Based upon the desired true correlation and accounting for error rates, an "observed" correlation can be derived that is tied to the number of sample pairs necessary.

#### **Background and Rationale**

## PM<sub>2.5</sub> DQO Process

DQOs are qualitative and quantitative statements that clarify the monitoring objectives, define the appropriate type of data, and specify the tolerable levels of potential decision errors that will be used to determine the quality and quantity of data needed to support decisions (i.e., NAAQS comparisons). A more complete description of the PM<sub>2.5</sub> DQOs and how they were derived is presented in Attachment B.

DQOs for PM<sub>2.5</sub> were developed during the months from April to July of 1997. A number of assumptions were made in order to generate realistic error rates. Table 6-1 provides a listing

of these assumptions. In 2001, EPA reassessed the assumptions underlying the 1997 DQOs. In almost all cases, the assumptions made in the 1997 process held true in the 2001 evaluation.

The PM<sub>2.5</sub> DQOs were generated using conservative but realistic assumptions. For example, the DQOs were generated assuming a sampling frequency of every 6 days with 75% completeness. This is the lowest sampling frequency allowed in the Code of Federal Regulation. A 95% confidence limit around the annual mean at this sampling frequency would be "wider" than a 95% confidence limit for an every day sampling frequency at 90% completeness. In all cases, the assumptions in Table 6-1 are close to the extremes of realistic and allowable data. Assumptions in bold are variables that will be discussed later in this section.

# **Table 6-1 2001 DQO Assumptions**

- 1. Bias is -10% or + 10%
- 2. Precision is 10%
- 3. Annual NAAQS is controlling standard
- 4. No spatial uncertainty and each monitor stands on its own (no spatial averaging)
- 5. 1 in 6 sampling with 75% completeness (144 days) (each of 12 quarters was rounded up to 12 samples per quarter)
- 6. 3-year annual average is truth, (every day sampling and 100% comp.) up to bias and measurement variability
- 7. Lognormal distribution for population variability, 80% CV
- 8. Normal distribution for measurement uncertainty
- 9. Seasonal ratio (ratio of avg conc for highest season to lowest season) = 5.3
- 10. No auto correlation in daily concentrations
- 11. Bias and measurement variability (precision) applies to entire 3 years
- 12. Type I and type II decision errors set to 5%

Figure 6.1 provides the power curve based on the 2001 assumptions shown in Table 6-1. A power curve is an easy way to display the potential of decision errors based upon the choice of

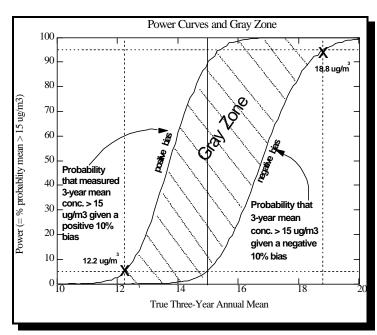


Figure 6.1 Power curve based on 2001 assumptions

various assumptions that affect data uncertainty. The gray zone is the range of concentrations for which the decision errors are larger than the desired rate of 5%.

Based on the 2001 assumptions, the gray zone is 12.2 to  $18.8~\mu g/m^3$ . This means that if all the 2001 assumptions hold, the decision maker has a 5% chance of observing a 3-year mean

concentration that is greater than 15  $\mu$ g/m<sup>3</sup> even though the true mean concentration is 12.2  $\mu$ g/m<sup>3</sup> (all assumptions and a 10% positive bias). As has been mentioned, the 2001 assumptions are realistic but conservative. For example the CY00 PM<sub>2.5</sub> QA Report demonstrates that the

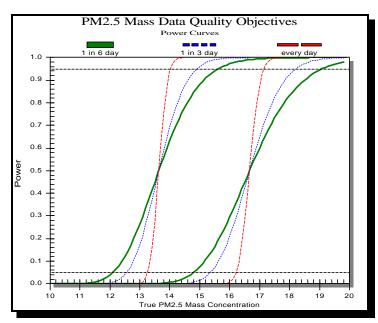


Figure 6.2. Annual standard power curve changes due to changes in sampling frequency

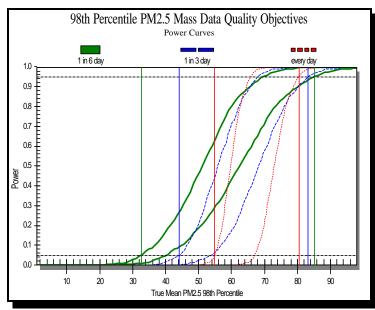


Figure 6.3 Daily standard power curve due to changes in sampling frequency

precision and bias estimates at a national level are within the DOOs. Assumptions that are "better" than those listed in Table 6-1 will tend to decrease the width of the gray zone. Figure 6.2 provides an example of the power curve/gray zone changes for a simple change in sampling frequency from 1 in 6 day (green/solid) to 1 in 3 day (blue/dots) to every day (red/dashed); all the other 2001 assumptions remain the same. Higher sampling frequencies result in narrower gray zones, meaning that decision errors are reduced. Using the same 2001 assumptions, generating a power curve for the daily standard would yield a gray zone of 32.4 to 86.0 ug/m<sup>3</sup> (see Figure 6.3).

Because the assumptions for any particular site will vary, OAQPS commissioned the development of a software tool to help Headquarters and State, local and Tribal organizations determine the potential for decision errors based on assumptions relevant for sites within their network. The tool is based on thousands of data simulations and produces approximate gray zones. Figures 6.2 (annual standard) and 6.3 (daily standard) are generated using this tool which allows for multiple scenarios (power curves) to be reviewed on one table. The assumptions listed in bold in Table 6-1 can be changed to suit a particular network. Furthermore, the tool was enhanced to include a daily air quality index (AQI) use and will be useful for making decisions about the acceptability of REMs or CACs within a network.

The PM<sub>2.5</sub> DQO evaluation showed that sampling frequency, population variability, completeness and measurement bias play a significant role in the width of the gray zone. Measurement precision did not have a significant effect on the gray zone for both the annual and daily standard which suggests more imprecision could be tolerated with little effect on decision errors.

# **Correlation Coefficient DQO Process**

A DQO type exercise was performed to determine the minimum correlation coefficient necessary between data from a PM2.5 continuous monitor and a collocated FRM. The data from the PM2.5 continuous monitor is used after a transformation has been made, if necessary. The DQO exercise is based upon identification of a true underlying relationship given the intended use of the data. Other information was considered such as the current national equivalency criteria; expected sample size of collocated continuous and FRM samplers; and performance of the current network (section 2). Correlations for CAC type continuous monitors are more flexible (less strict) than REM type monitors since CAC monitors are not to be used for NAAQS decisions.

Test criteria for PM2.5 class III equivalent methods (which would include PM2.5 continuous monitors) have never been published. The current national equivalency criteria for PM10 and PM2.5 Class I and II monitors identifies a correlation of >= 0.97 based upon a minimum number of 10 sample pairs at each test site. A correlation of  $\geq 0.97$  is expected to be too difficult for most PM2.5 continuous monitors and may not even be necessary. More relaxed minimum correlation criteria can be postulated based upon two important differences between how the traditional equivalency program works and how a process for approval of REM and CAC type monitors is proposed. First, while the national equivalency program requires at least 10 valid sample pairs per site, the REM and CAC process is expected to generate many more sample pairs. This is primarily based upon the expected sample frequencies of collocated FRM samplers and a years worth of data. By having a larger number of sample pairs, more confidence in the "true" underlying correlation can be determined. Second, in the national equivalency program there is a high degree of intra-method collocation required. When the precision of the FRMs are not acceptable, that sample set is discarded. In the testing proposed in this document limited collocation is required and no provisions for invalidating a sample set is provided for based upon poor precision. This has the effect of potentially keeping FRM values that lead to a degradation of the correlation in the sample set. One of the merits of the REM and CAC process is that the testing of the instruments takes place under typical field conditions for which the monitors are to be approved. A reduction in the requirement for correlation is therefore balanced against use of a substantially larger number of sample pairs and a more "typical" FRM data set.

Identification of true underlying correlations for each category of PM2.5 continuous monitors were made. For a CAC category, a true underlying correlation less than or equal to the square root of 0.7 was chosen. For a REM a true underlying correlation less than or equal to the

square root of 0.8 was chosen. These true underlying correlations are based upon an iterative process of evaluating the error rates and sample sizes needed for a reasonable observed correlation. Error rates include an alpha, beta and delta. The alpha is the chance of incorrectly concluding that the correlation between the transformed continuous and FRM data is good enough to be used when in fact the correlation is not good enough. Since one of the monitoring objectives for the REM is attainment decisions, a high alpha will be chosen to protect against using a model where the true underlying correlation is not good enough. The beta is the chance of concluding that the correlation between the transformed continuous and FRM data is not good enough when in fact it is. The problem with this type of decision is that one would work on improving the method or model relating the continuous monitor and FRM when in fact the model is already good enough. The delta is the size of the gray region.

The derivation of the data in this section is based on work documented in "Using Continuous PM2.5 Monitoring Data to Report an Air Quality Index," *J. Air & Waste Manage*. *Assoc.* **52**:104-112, January 2002. NOTE: In a previous application of the technique for public reporting (see Appendix C), only the tables for  $R \le \operatorname{sqrt}(0.60) = 0.77$  were provided. This is because the decision makers working on the DQOs for using continuous data to report the AQI decided that  $R \le 0.77$  was sufficient. For more uses of the data, it likely is prudent to test for higher true, underlying correlations, hence 2 new sets of tables are provided below.

Another note. Sample sizes less than 20 should not be used. The reason for this is that the primary assumption behind the equations used to generate the values in the tables is that W=0.5\*ln((1+R)/(1-R)) is approximately normally distributed. This assumptions appears not to be valid for sample sizes less than 20 and possibly not for sample sizes less than 30. Sample sizes less than 20 are shown but crossed off in the tables 6-2 and 6-4.

A final note. The sample sizes and R<sup>2</sup> in the tables have changed from those developed for the AQI DQOs. There was an error in the equations in the original derivation. That error has been corrected and the correct values are reflected in the tables below. The correction has had the effect of reducing the required number of pairs of data needed for evaluating the correlation.

## **Correlation for CAC category of Continuous Monitors**

If the intended use of the data is for monitoring objectives other than comparison to the NAAQS a recommendation is made to test to see if the true underlying correlation is <= square root (0.7) = 0.84. For error rates a recommendation is made for a gray zone of square root (0.7) to square root (0.85) meaning delta of 0.15, alpha should be 0.05 and beta should be 0.2. This results in a **minimum sample size of 44 and a minimum correlation 0.90** (square root 0.81). This sample size represents a site operating a FRM on a 1 in 6 sample schedule at 75% completeness for a year. If more sample pairs are used then a lower observed correlation may be permissible given the same error rates.

Table 6-2. Lower Bound for Sample size requirements for model development by ", \$, and ) under a null hypothesis of  $H_0$ : R # sqrt(0.7) = 0.84

Size of Gray	Size of Gray Region ()  False Acceptance Decision Error (\$)	False Rejection Decision Error (")		
Region ()		0.05	0.01	
	0.3	<del>16</del>	25	
0.20	0.2	20	31	
	0.1	27	39	
	0.3	34	56	
0.15	0.2	44	69	
	0.1	59	88	
0.10	0.3	90	152	
	0.2	117	187	
	0.1	160	242	

**Table 6-3.** Lower bound on observed model R<sup>2</sup> value (for above sample size) necessary for concluding model adequacy by ", \$, and ) under a null hypothesis of  $H_0$ : R # sqrt(0.7) = 0.84

Size of Gray	False Acceptance Decision Error (\$)	False Rejection Decision Error (")		
Region ())		0.05	0.01	
	0.3	0.87	0.88	
0.20	0.2	0.85	0.86	
	0.1	0.83	0.85	
	0.3	0.82	0.83	
0.15	0.2	0.81	0.82	
	0.1	0.79	0.81	
0.10	0.3	0.78	0.78	
	0.2	0.77	0.78	
	0.1	0.76	0.77	

## **Correlation for REM category of Continuous Monitors**

If the intended use of the data is for monitoring objectives to include comparison to the NAAQS a recommendation is made to test to see if the true underlying correlation is <= square root (0.8) = 0.89. For error rates a recommendation is made for a gray zone of square root (0.8) to square root (0.90) meaning delta of 0.10, alpha should be 0.01 and beta should be 0.1. This results in a minimum sample size of 96 and a minimum correlation of 0.93 (square root 0.87). This sample size represents a site operating a FRM on a 1 in 3 sample schedule at 80% completeness for a year. If more sample pairs are used then a lower observed correlation may be permissible given the same error rates.

**Table 6-4.** Lower Bound on Sample size requirements for model development by ", \$, and ) under a null hypothesis of  $H_0$ : R # sqrt(0.8) = 0.89

Size of Gray	False Acceptance Decision Error	False Rejection Decision Error (")		
Region ())	(\$)	0.05	0.01	
	0.3			
0.20	0.2			
	0.1			
	0.3	<del>12</del>	<del>19</del>	
0.15	0.2	<del>15</del>	22	
	0.1	<del>19</del>	28	
0.10	0.3	37	61	
	0.2	48	75	
	0.1	64	96	

Table 6-5. Lower bound on observed model  $R^2$  value (for above sample size) necessary for concluding model adequacy by ", \$, and ) under a null hypothesis of  $H_0$ : R # sqrt(0.8) = 0.89

Size of Gray	Size of Gray Region ()  False Acceptance Decision Error (\$)	False Rejection Decision Error (")		
Region ())		0.05	0.01	
	0.3			
0.20	0.2			
	0.1			
	0.3	0.93	0.93	
0.15	0.2	0.92	0.93	
	0.1	0.91	0.92	
0.10	0.3	0.88	0.89	
	0.2	0.87	0.88	
	0.1	0.86	0.87	

# **CONCLUSIONS FROM DQO TOOL**

The PM<sub>2.5</sub> mass DQOs were developed for making decisions about the 3-year average of annual means, since the annual standard is the controlling standard. In particular, they were developed to evaluate the chance of concluding an average concentration was above 15 : g/m³, when in truth it was not, and the chance of concluding an average concentration was below 15 : g/m³, when in truth it was not. Due to the minimum number of measurements that go into the 3-year average of annual means (at least 144), it is easy to see why measurement precision does not have a large influence on the size of the gray zone of the power curve. However, data uses that involve no averaging, such as real-time reporting like the AQI, are more sensitive to measurement imprecision. Thus, caution should be exercised in drawing conclusions from the DQO power-curve tool for uses other than those for which it is currently designed. If the assumptions are not appropriate or if the data use is different than comparison to the standards, the power curves and

gray zones likely do not reflect the true decision errors. However, the tool is extremely useful in showing the effects of various types of population and measurement uncertainties on decision errors.

The software tool is available on the AMTIC PM<sub>2.5</sub> Website. In addition, we hope to be able to develop a report in AIRS that would automatically generate the DQO assumptions listed in Table 6-1 by a variety of data aggregation schemes (i.e., reporting organization, by a collection of sites etc.)

# Acceptable Performance Criteria for Continuous Monitoring Using Power Curve Tool

Figure 6.1 set up the most extreme case that is tolerated in the  $PM_{2.5}$  DQO, based on the assumptions in Table 6-1. The DQOs have associated with them a gray zone which will be used to develop acceptable bounds for the quality of the data required (REM) or recommended (CAC) for the continuous monitoring program. An important note is that the data for which the quality is being evaluated is not the raw data produced by the continuous monitors. Rather it is the continuous data that has been transformed, using a statistical model, to be FRM like. A description of the transformations and applicability to REM and CAC is described in section 7.

Table 6-6 summarize the assumptions for a REM and CAC, as it pertains to data use, allowable transformations, and data quality requirements or goals.

Table 6-6 Summary of assumptions for REM and CAC

REM	CAC
Assumptions: Will be used in comparison to NAAQS Must have FRMs in Network Can include transformations with one or more variables so long as each variable can be controlled Must meet 1-3 day DQO (gray zone) but specifically meet 10% bias DQO and correlation coefficient of 0.93.	Assumptions: Will not be used in comparison to NAAQS Must have FRMs in Network Can include complex transformations Should meet 1-6 day DQO (gray zone) but specifically meet 10% bias DQO and correlation coefficient of 0.9

Developing performance criteria using the power curve tool is a multi-step process. The first step is to collect information from the CAC/REM network. The second step is to develop a transformation that produces FRM-like data from the CAC/REM (details of which are provided in Section 7). The third step is to determine the spatial extent for which the transformation is appropriate (details of which are provided in Section 9). The fourth step is to determine reasonable values for the highlighted parameters in Table 6-1. The values should be reflective of the entire spatial extent of the CAC or REM network being evaluated. The last step is to use the DQO software tool to determine the gray zone that results from the values from the previous step. If the bias is within -10% and +10%, the gray zone is within 12.7 and 18.1 : g/m³ (the gray zone for an FRM that operates every third day) and the correlation between collocated FRMs and continuous monitors is at least 0.93 and is based on at least 96 pairs, then the continuous sampler meets the requirements for being a REM. If the bias is within -10% and +10%, the gray zone is

within 12.2 and 18.8 : g/m³ (the gray zone for an FRM that operates every sixth day), and the correlation between collocated FRMs and continuous monitors is at least 0.90 and is based on at least 44 pairs then the continuous sampler meets the goals for being a CAC.

Figure 6.4 provides an example of the power curve for a 3-year mean based on the following data quality input parameters:

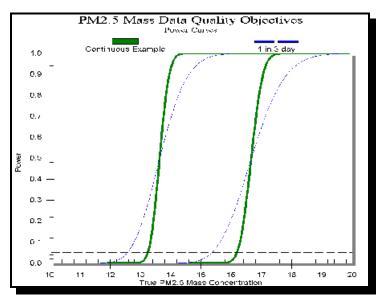


Figure 6.4. Example continuous monitoring network power curve relative to 1 in 3 day power curve.

<	bias	10%
<	completeness	75%
<	sampling frequency	every day
<	measurement CV	30%
<	population CV	80%
<	Seasonal ratio	5.3

The resultant gray zone is 13.2 µg/m³ (lower left line green solid) and 17.1 µg/m³ (upper right line green solid which is within the 1-3 day DQO of 12.7 (lower left blue dashed) and 18.1 (upper right blue dashed). Therefore, this example continuous monitoring network could be considered acceptable for CAC or REM designation.

#### **Simplified Performance Criteria for Continuous Monitoring**

Organizations may use the DQO process described above to determine levels of measurement imprecision that can be tolerated but still provide data of a quality to support decisions about comparison to the NAAQS. For organizations not interested in using the DQO tool to develop gray zones applicable to specific areas, the DQOs are set to 20% measurement CV, bias within -10% and +10%, and correlation greater than 0.93 for REM and 0.90 for CAC. REMs are required to meet these objectives whereas it is highly recommended that CACs meet these objectives.

# Summary of Performance Criteria for PM<sub>2.5</sub> Methods

When discussing performance criteria, it's important to clarify the difference between acceptance of a method in the designation process and the on-going performance based goals. The acceptance of a method in the designation process is associated with the Reference and Equivalency program defined in 40 CFR Part 53. This process is purposely strict in order to assure the quality of data when subsequently designated methods are used throughout the country. Table 6-7 summarizes each category of existing and potentially revised methods with criteria for acceptance of the method and criteria for the on-going evaluation of the performance of that

method.

Table 6-7. Performance Specifications for PM2.5 Methods

Category of Method	Requirements for Acceptance of Method	Existing Performance Goal for Acceptable Measurement Uncertainty	Future Performance Goal for Acceptable Measurement Uncertainty
FRM	Many design and performance criteria. Precision for field testing: $<2~\mu g/m^3~when~concentration~is <40~\mu g/m^3~(24~hour~sample)~or <30~\mu g/m^3~(48~hour~sample); Rpj <5\%~for~concentration > 40~\mu g/m^3~(24~hour~sample)~or >30~\mu g/m^3~(48~hour~sample).$	10% coefficient of variation (CV) for total precision and +/- 10 percent for total bias.	No Revision
FEM	Across a limited number of field test sites depending on class of equivalency: Slope of 1+/- 0.05 Intercept of 0 +/- 1 $\mu$ g R \$ 0.97	10% coefficient of variation (CV) for total precision and +/- 10 percent for total bias.	No Revision.
REM	Within each network that is being considered: 20 % coefficient of variation (CV) for total precision and +/- 10 percent for total bias and correlation coefficient of \$ 0.93.	NA	Utilize 1 in 3 day DQO/Powercurve or simplified approach of 20% coefficient of variation (CV) for total precision and +/- 10 percent for total bias and correlation coefficient of \$ 0.93.
CAC	Within each network that is being considered: 20 % coefficient of variation (CV) for total precision and +/- 10 percent for total bias and correlation coefficient of 0.9 (Goal, not requirement.)	NA	Utilize 1 in 6 day DQO/powercurve or simplified 20% coefficient of variation (CV) for total precision and +/- 10 percent for total bias. (Goal, not requirement.) And correlation coefficient of \$ 0.90

# Section 7. Data Transformation Policy and Guidance

Variations in  $PM_{2.5}$  measurements attributed to methodological differences should be minimized to support consistent data analysis across temporal and spatial regimes. For example, it would be erroneous to infer that 20% of the  $PM_{2.5}$  measured in an urban area is due to local sources based on a comparison of the concentrations measured by monitors in an urban area to concentrations from upwind sites, if the instrumentation at the upwind sites are biased low by 20%, relative to the instrumentation used in the urban area. Realistically,  $PM_{2.5}$  measurements should "look" like measurements taken by an FRM. This is because of the richness of the available FRM data base and due to the difficulty in ascribing a "reference" check for aerosol measurements.

Non-FRM samplers generally operate at a higher temporal resolution than FRMs and many will operate where there is no FRM, thus helping to fill spatial gaps in the FRM network. However, to be able to use data from multiple types of  $PM_{2.5}$  mass monitoring networks (FRM, non-FRM) in the same analysis, the data must be comparable. Comparable means that if the various samplers were spatially and temporally interchanged, approximately the same concentrations would be measured. To achieve comparability, it is possible to transform, using statistical models, non-FRM data to look like FRM data or vice versa. Due to the interest in FRM-like concentration surfaces, the remainder of this section will only address transforming data from non-FRM samplers to produce FRM-like measurements.

Due to the inherent differences in measurement principles between FRM and PM continuous monitors there may be biases between the measurements obtained from an FRM and continuous monitor. If the bias is consistent through time and across space, a standardized correction factor could be used to produce FRM-like measurements from the continuous monitors. However, since mass concentration and composition and environmental conditions vary, a standard correction may not be practical on a national scale but may be achievable on a more regional scale. This section provides information about the development of transformations to produce FRM-like measurements from continuous measurements.

Based on preliminary analyses summarized in Section 2, developing a statistical model to relate concentrations from continuous samplers (predominantly TEOM's) to FRM samplers is achievable, although the complexity of the model varies by location and may vary through time. The complexity likely is a function of the stability of the composition of the aerosol, the stability of the meteorology (temperature and humidity), and the continuous monitoring methodology. The following guidance for developing transformations is based on the experience gained in analyzing the limited collocated FRM/continuous database to date. The database is limited due to temporal representativeness (at best 2 years since the FRM network was deployed in 1999), spatial representativeness (continuous samplers have been and continue to be deployed predominantly in large urban areas), and non-FRM sampling techniques. The database is predominantly based on data reported to AIRS. Prior to 2000, it was not possible to determine whether the data from a continuous monitor was reported after being adjusted by "correction" factors. Beginning in 2000, AIRS method codes were expanded so that it would be possible to determine whether correction factors had been applied, although it is not possible to specify the form or parameter estimates of

the adjustment. These new method codes appear not to be accurate for all sites, as seen in Section 2, making it a further challenge to determine appropriate transformations.

A balance between forcing a particular measurement principle to mimic another (i.e., the FRM) is a significant complication that must be recognized in this task. The practical needs for data analysts demand some level of comparability. However, there is intrinsic value in the very differences that emerge between measurement systems due to the complex character of aerosols. The intention clearly is not to define the FRM as truth, but rather to recognize the practicality of the existing network. These considerations of basic measurement principles are embodied in this transformation guidance. Where relationships between two measurement systems exhibit simple linear and constant character, one can probably assume the difference in measurement approach does not result in a significantly different indicator of ambient aerosol. Such simple relationships are the foundation for accommodating REMs that can be compared to the NAAQS. Variables that can be controlled such as ambient temperature are also permissible in a multi-variate REM model. On the other hand, more complex relationships between a candidate system and the FRM suggest that a significantly different aerosol property is being accounted for (likely varies over time or space) in one system relative to the other. This does not mean one system is superior to the other, but reasonable judgement suggests a limit to forcing a system to mimic the FRM for regulatory use, but to accommodate the system for other data uses within the limits of data comparability guidelines. This latter approach reflects the concept underlying the expanded use of CAC's.

The guidance on transformations will be broken into two sections, one for the CAC and one for the REM. The guidance for acceptable transformations for REM's will be strict and limited to transformation models where each variable can be controlled. Acceptable transformations for CAC's will be less strict. For either case, recall that the performance criteria presented in Section 6 is based on the transformed continuous measurements. Note that if the performance criteria are met with the raw continuous measurements, then no transformation is required. That is, transformations need not always be developed.

Regardless of whether the continuous sampler is a CAC or REM, measurements should be reported to AIRS. Given that data users might not understand the differences in the sampling methodologies, it is recommended that the data be entered AFTER applying a transformation to produce FRM-like measurements. However, it will be important for other data uses to know what transformations have been applied. EPA will be investigating possible ways to include the transformation information in AIRS so that it will be possible to "back out" the transformation and have the original, non-FRM measurements.

# Transformation Guidance for CAC

Even though the data from a CAC will not be used for direct comparison to the NAAQS, they should meet the performance criteria as described in Section 6. Although this is not a requirement, it is strongly recommended for comparability of measurements across the network. The data used for evaluation in the DQO process are those that have been transformed to be FRM-like; that is, the DQO's are not necessarily based on the raw data from the non-FRM's. This section describes the process for developing the transformations for CAC's. The rationale and details for the selection of many of these criteria are included in the EPA document *Reporting an Air Quality Index (AQI) Using Continuous PM*<sub>2.5</sub> *Data: Data Quality Objectives (DQOs) and Model Development for Relating Federal Reference Method (FRM) and Continuous PM*<sub>2.5</sub> *Measurements (Attachment C)*.

- Step 1. Create daily non-FRM measurements. If the non-FRM data are collected more frequently than daily, the sub-daily intervals should be averaged before comparing to the FRM data. At least 75% of the sub-daily intervals should be valid to consider the average to be valid. Also, the sub-daily intervals to be averaged should be those that most closely span midnight to midnight, the operating interval of the FRM's.
- Step 2. Determine if there are sufficient data to develop statistical model. The model to relate the non-FRM and FRM data should be based on data from all four seasons and have at least 44 valid pairs of data, approximately evenly distributed through each season. It is recommended that each season have at least 11 valid pairs. If there are not more than 44 valid pairs approximately evenly distributed through the seasons, it is recommended that additional data be collected. The 44 pairs need not be from only one year.
- 3. Develop a statistical model. The statistical model relating the non-FRM and FRM data should have the FRM data as the response variable (also called the dependent variable) and minimally must include the non-FRM measurements from Step 1 as an explanatory (independent variable). The number and type of explanatory variable allowed in unlimited. The model can be based on the data as is or can be based on the natural logarithms of the data. The final R<sup>2</sup> between the measured and predicted FRM measurements should be 0.81 or greater (corresponding to a correlation of 0.90 or better).
- 4. Spatial extent for use of one transformation. Section 8 describes the process for determining the area within which one transformation may be used for all of the continuous samplers, regardless of whether the continuous sampler has been previously collocated with an FRM.
- 5. On-going evaluation of transformation and its spatial extent. The statistical model should be revisited every 3 years, or more frequently if there is reason to believe a change in the relationship between the non-FRM and FRM may have occurred. Possible reasons for such changes include, but are not limited to, a change in sampling methodology, change in aerosol composition due to control strategies, or different meteorological regimes than what was observed during the development of the statistical model. If a new statistical model is more appropriate, that model should be used from that date forward. That is, one model would be used up to one date and the

next model would be used for subsequent dates.

# Transformation Guidance for REM

The data from REM's must meet the performance criteria as described in Section 6. The data used for evaluation in the DQO process are those that have been transformed to be FRM-like; that is, the DQO's are not necessarily based on the raw data from the non-FRM's. This section describes the requirements for the transformations. Because the data are intended to be used for NAAQS comparisons, the allowable statistical models and parameter estimation will be explicitly defined. The guidance components are as follows.

- Step 1. Create daily non-FRM measurements. If the non-FRM data are collected more frequently than daily, the sub-daily intervals should be averaged before comparing to the FRM data. At least 75% of the sub-daily intervals should be valid to consider the average to be valid. Also, the sub-daily intervals to be averaged should be those that most closely span midnight to midnight, the operating interval of the FRM's.
- Step 2. Determine if there are sufficient data to develop statistical model. The model to relate the non-FRM and FRM data should be based on data from all four seasons and have at least 91 valid pairs of data, approximately evenly distributed through each season. It is recommended that each season have at least 20 valid pairs. If there are not more than 90 valid pairs approximately evenly distributed through the seasons, it is recommended that additional data be collected. The 91 pairs need not be from only one year.
- Step 3. Develop a statistical model. The statistical model relating the non-FRM and FRM data should have the FRM data as the response variable (also called the dependent variable) and minimally must include the non-FRM measurements from Step 1 as an explanatory (independent variable). One or more additional explanatory variables are allowed so long as the variable(s) can be controlled. Examples of additional exploratory variables that can be controlled include ambient temperature and barometric pressure as these variables are used for active flow control on most monitors. Variables such as Julian date or using multiple models above and below a specific temperature or concentration are also permissible. The model can be based on the data as is or can be based on the natural logarithms of the data. The final R<sup>2</sup> between the measured and predicted FRM measurements should be 0.87 or greater (corresponding to a correlation of 0.93 or better).
- Step 4. Spatial extent for use of one transformation. Section 8 describes the process for determining the area within which one transformation may be used for all of the continuous samplers, regardless of whether the continuous sampler has been previously collocated with an FRM.
- Step 5. On-going evaluation of statistical model and its spatial extent. At least 30% (rounding up) of the non-FRM sites must be permanently collocated with FRMs to provide the data needed to evaluate regularly the reasonableness and consistency of the transforms. The collocated sites should be distributed to represent different composition and meteorological regimes. The

statistical model should be revisited every 3 years, or more frequently if there is reason to believe a change in the relationship between the non-FRM and FRM may have occurred. Possible reasons for such changes include, but are not limited to, a change in sampling methodology, change in aerosol composition due to control strategies, or different meteorological regimes than what was observed during the development of the statistical model. If a new statistical model is more appropriate, that model should be used from that date forward. That is, one model would be used up to one date and the next model would be used for subsequent dates.

#### **Section 8. Defining Regional Applicability**

The basic relationship between a continuous monitor and an FRM should be similar throughout a given "region" of application, especially with respect to bias. This reasoning is the foundation for the new regional equivalent method approach which assumes consistent monitor behavior can be achieved within a "region" despite inconsistencies nationally. Sections 3 and 4 provided example requirements (minimum 2 sites per MSA) for demonstrating consistency. The determination of regional applicability should be based first on technical considerations related to the consistent performance of a candidate continuous method. This section addresses approaches to determine regional applicability, and is intended to raise the understanding of this topic for further development of applications guidance.

Operationally, only one transformation model would be applied within the region of consideration. Determining the region in which the use of one transform is appropriate, meaning that all the sites within the region will meet the bias, precision and correlation requirements (REM) or goals (CAC), can be approached in two ways. One approach is to establish regions a priori where the regions explicitly cover specific land masses in the United States. For example, regions may be the interior southeast, the east coast, Florida, the industrial belt, the Midwest, the western coast, the arid Southwest, Alaska, the Rocky Mountain States, and the humid northwest coastal area. The testing requirements for a candidate method would have to be met throughout one or more of these previously established regions. If one of the sites does not meet the testing requirements, then the method can not be used within that region. Such an approach implies knowledge about areas in which a particular type of continuous methodology and the FRM's have similar relationships. As shown in Section 2, knowledge based on the analysis of ambient measurements does not currently exist due to lack of data, especially data from emerging continuous monitoring methodologies. However, as more ambient measurements are collected for the various continuous monitoring methodologies, environmental conditions, and particulate composition and size distributions, such regions may become more clearly defined. EPA and other organizations (monitoring agencies, Tribal nations, Regional Planning Organizations [RPO's]) would address logistical and administrative complications associated with multiple monitoring organizations operating in a defined "region."

A second approach is to allow any size and shape of region. The State/local/Tribe, RPO, or vendor interested in using a particular type of continuous instrument would specify the boundary of the region and then follow the testing requirements or goals to prove whether one transformation would be adequate for the entire region. This may follow established geo-political boundaries such as a State including all local monitoring agencies or multiple cooperating states. The domain of the region is flexible. However, once the testing has been completed for a specific domain, the domain remains fixed until on-going evaluations indicate the performance criteria are no longer being met throughout the region or additional testing supports extending the region of approval.

It will be strongly encouraged that potential continuous monitoring methodologies be deployed at a core set of sites where the data from these sites will help to determine potential regions for the first approach. Until there are sufficient data to determine appropriate regions, the second approach will be used.

# Definition of Regionality of Transformation

For a specific type of continuous monitoring methodology, given a sufficiently dense monitoring network of these monitors collocated with FRM's, it would be possible to develop a surface of the bias between the two types of instruments. In some places, the bias might be small while in other places the bias might be large. In some places, the bias might be negative and in others, it might be positive. Hopefully, the surface of biases would be smooth, that is, it would gradually change from one location to the next. Given such a smooth surface, it would be possible to produce FRM-like measurements at any location, even if there were no collocated FRM.

A difficulty with this construct of a surface of biases is that there is not a sufficiently dense network with which to build a surface for any large geographical area, especially for each type of continuous monitoring methodology. However, understanding this surface is the basis for being able to know sizes of regions. Collection of data with which to build such a surface is an important step to understanding regionality and is described below.

A surface of biases implies that the transformation to generate FRM-like measurements from continuous data would vary from site to site. Implementing site-specific transformations likely would prove to be intractable for a large number of sites, especially if the transformation is considered to be part of the method. One way around this problem is to use one transformation over an area where the biases are "similar." Specifically, the definition of the regionality of a transformation is that geographical area in which it is possible to use one statistical model to estimate FRM-like measurements and those FRM-like measurements meet the performance criteria specified in Section 6. This may possible in a modified geographical approval for a method where small cities and rural areas are approved for a method but larger cities are not. This might be necessary when small cities and rural areas encounter a relatively stable aerosol leading to little bias on a continuous instrument while larger cities encounter a higher fraction of unstable aerosols leading to unacceptable levels of bias on a continuous instrument. Determining regions for which biases are "similar" also hinges on a dense data base of collocated FRM's and continuous instruments.

## Data Collection to Support Definition of Regionality of Transformations

At least 100 sites of collocated continuous monitors and FRM's will be established as part of a National Core (NCore) network. These collocated sites will provide the data necessary to understand and monitor the temporal and spatial relationships between FRM's and continuous samplers. Characteristics of the sites include: (1) FRM's should operate at least every third day; (2) monitors should operate year-round and every year; (3) speciation trends sites are ideal given that the speciated data may help better understand the relationships; and (4) sites upwind of the speciation trends sites are also ideal, as the upwind sites likely have different compositions due to urban/rural gradients. The database generated by these sites will be regularly analyzed to determine if and how the FRM-continuous relationships vary spatially and temporally and how those relationships may change over time as compositions change due to implemented control strategies.

Until such time that a priori regions are defined, the regions may be any size and shape and the following guidance is applicable.

## Regionality of Transformations for CAC

If the data from the non-FRM's are intended to be used for nonregulatory purposes, it is important that the data be comparable to the data produced by FRM's. However, since the data will not be used for direct comparison to the NAAQS, there is more flexibility in determining the regions within which one transformation is applicable.

- Step 1. Develop transformations for each collocated site within the region of interest, based on the guidance provided in Section 7.
- Step 2. Determine whether the transformations are statistically equivalent. For the sites that are equivalent, pool their data together to estimate one transformation. This one relationship should be used at each of the sites that was considered equivalent and may be used at other continuous sites for which there is no collocated FRM, provided that the sites operate the same type of non-FRM sampler using the same standard operating procedures, have similar chemical composition, and are exposed to similar meteorology. For examples, it would be inappropriate to apply a relationship established at a site running a TEOM to a site running a BAM, to apply a relationship established at a population-oriented site without any nearby sources to a site impacted by a large local source, or to apply a relationship established at an inland site to a coastal site. Sites that are not statistically equivalent to others should be considered unique, meaning that the transformation for the site should not be applied to any other site.
- Step 3. On-going evaluation. It is recommended that at least 10% of the non-FRM sites be collocated with FRM's for at least 1 year of every 3 years and that the regionality be re-evaluated every 3 years. This recommended level of collocation on a permanent basis generally is met or exceeded in current networks.

#### Regionality of Transformations for REM

Following the approaches for CAC and REM discussed in Section 4, the approval process for regional applicability for REM's would be considered part of the method. The method approval process would follow the same process for review and approval as other candidate federal equivalent methods.

#### Section 9. Monitoring Methods Guidance and Support

Despite a substantial allocation of resources in overall PM monitoring implementation, very little methods development work has been performed in the area of PM<sub>2.5</sub> continuous monitors. This lack of development combined with requirements for lengthy field testing in multiple sites and high statistical correlations for designation as a PM<sub>2.5</sub> Federal Equivalent Method (FEM) have resulted in no applications for designation of continuous PM<sub>2.5</sub> monitors as FEM.

#### **Introduction:**

During the planning stages of the PM<sub>2.5</sub> monitoring program there was little emphasis on development of PM continuous methods by EPA. There were no nationally coordinated field testing programs to assess the usefulness of continuous methods over a variety of locations and aerosols. A guidance Document was written in 1998 compiling the available field testing on PM continuous methods to date; however, this document offered little insight on planning a long term strategy of using PM<sub>2.5</sub> continuous methods for regulatory purposes. Additionally, EPA never actually proposed or promulgated Class III equivalency criteria that would provide the testing requirements for PM<sub>2.5</sub> continuous methods. Since no criteria have ever been proposed there has never been an opportunity for the various stakeholders in the monitoring community to provide comments on the usefulness of the Class III equivalency testing criteria. There is an expectation that the equivalency criteria for Class III designations would be at least as strict as the Class II criteria. But since these criteria have never been published by EPA there is no clear path for acceptance of PM<sub>2.5</sub> continuous methods. Without EPA directly involved in developing PM continuous methods, vendors have been left to pursue improvements on their own. While some vendors have been successful at improving their methods by working directly with the States, these methods have not been appropriately tested on a national scale. For instance, the California Air Resources Board (CARB) has been working with the Met One Beta Attenuation Monitor over the last few years, yet very little data exists on this method collocated with FRM's in any east coast States. Also, Rupprecht & Patashnick Company have commercialized the SES as an add on to the TEOM PM continuous monitor to allow for operation of this instrument at lower temperatures; however, little information is known about the long-term usefulness of the SES. The result of all of this is that there are no designated equivalent methods for PM<sub>2.5</sub> continuous monitors. Also, little information is available in the form of peer reviewed field studies over a variety of methods and locations. Despite all these issues there is still a great deal of information to glean from monitoring agencies and vendors on how these methods may be best suited for implementation in routine regulatory networks. This section attempts to summarize a number of points in how to best set-up and operate PM<sub>2.5</sub> continuous monitors. Many of these suggestions have already been incorporated into commercially available monitors. None of the suggestions should be considered as "required" since ultimately the best measures of success are performance of the PM<sub>2.5</sub> continuous monitor with respect to its ability to reproduce itself (measurement precision) and comparison to a FRM (bias).

## Recommendations for Design and Operation of PM<sub>2.5</sub> Continuous Methods

In order to design an appropriate configuration for a  $PM_{2.5}$  continuous monitor, many issues need to be addressed. This section attempts to provide the general specifications for  $PM_{2.5}$  continuous methods. A detailed accounting comparing the FRM design and performance specifications with applicability to a generic  $PM_{2.5}$  continuous monitor follows.

# Comparing FRM and Continuous Methods for Design and Performance Criteria

The FRM is based upon both design and performance criteria as identified in 40 CFR, Part 50, Appendix L. Design criteria are applicable to components of the reference method such as the inlet and second stage separation device. Performance criteria are applicable to things such as the control of flow rate and maximum allowable temperature difference between the filter and the ambient temperature. For any potential continuous method to be used in the routine regulatory network only performance criteria with respect to the comparison of collocated FRM and continuous data are to be used. However, the performance of a continuous method may be expected to be optimized by adhering to as much of the reference method as practical. In reality, many aspects of the design and performance of the FRM will not be included in a continuous methods operation due to the measurement principle of the instrument or other factors. For instance, much of the laboratory FRM criteria are not practical since there is not expected to be any pre or post-sampling gravimetric analyses in the traditional sense. This section discusses the current understanding of the FRM design and performance criteria that may be applicable to a potential continuous method for use in a regulatory network. Also, where applicable, alternatives to the design and performance criteria of the FRM are included as may be appropriate for use with continuous methods. This section is intended to provide information on how a continuous method might best be designed so that resulting data mimic that of the FRM. Due to the inherent operation of any one continuous method, many of the FRM design and performance criteria may not be suitable for inclusion in its design; therefore, none of the FRM criteria are required. Also, improvements to a design or performance criteria of the FRM are encouraged where appropriate in order for resulting PM continuous data to match that of the FRM.

## **General Specifications**

There are many specifications listed in the FRM as detailed in 40 CFR, Part 50, Appendix L. Among the general specifications, a number of items may be applicable to PM continuous monitoring. This section details those general provisions of the FRM that should be included in the design of a PM continuous method:

- *Pollutant* Fine particulate matter having an aerodynamic diameter less than or equal to a nominal 2.5 micrometers in the ambient air. Surrogates of this are possible if they result in meeting the necessary performance standards identified in section 6 of this document.
- *Units* Provide for data to be reported in units of micrograms per cubic meter. This may be calculated directly or indirectly through use of other inputs.
- *PM*<sub>2.5</sub> measurement range Provide for a lower and upper concentration limits that allow for meaningful comparison to the FRM. While the FRM is estimated to have a lower concentration limit of at least 2 ug/m³ and upper concentration limit of at least 200 ug/m³, continuous methods may be able to operate over an even wider range of concentrations. Most importantly, PM continuous methods need to provide concentration values in the environments they operate in. For instance, in an extremely dirty environment, a continuous method may be able to operate above 200ug/m³, if designed appropriately. Similarly, when a continuous method is operated at a very clean site the performance of the instrument should be able to discern changes in ambient PM<sub>2.5</sub> even over very low concentrations.
- Sample Period Provide for a sample period that can be used to calculate the midnight to midnight 24-hour average PM<sub>2.5</sub> concentration. For all other criteria pollutant continuous data the reported averaging period is usually 1-hour. Depending on the measurement precision of the PM continuous instrument an averaging period of more than one hour may be necessary. Therefore, while 1-hour averages should be capable of being reported; longer averaging periods may be necessary depending on the measurement precision of the instrument.
- Accuracy and Precision Because of the size and volatility of the particles making up ambient PM vary over a wide range and the mass concentration of particles varies with particle size it is difficult to define the accuracy of PM<sub>2.5</sub> measurements in an absolute sense. The accuracy of PM<sub>2.5</sub> measurements is therefore defined in a relative sense, referenced to measurements provide by the FRM. Section 6 defines the performance standards for PM<sub>2.5</sub> continuous methods.

## **Design Criteria**

Design criteria for the FRM are largely associated with the inlet and separation device to obtain the desired size selection of aerosol in the sample stream. Many of these criteria can be applied to a potential continuous method. Most of the commercial vendors of PM continuous methods have already incorporated these design criteria into their instruments. The table below describes the various design criteria for the FRM and their applicability to PM continuous methods. Also, where appropriate, alternatives to the FRM design criteria are offered:

Design Areas	Section of	FRM specification	Applicability to Continuous
	Appendix L		Methods

Inlet Assembly	7.3.2	PM <sub>10</sub> head with dimensions as described in figures L-2 through L-18. Use of louvers is recommended, but not required.	This should be applicable to most PM continuous methods
Downtube	7.3.3	With dimensions as described in figure L- 19	This may or may not be applicable to a PM continuous method. A downtube may not be needed if there is sufficient clearance for the PM 10 head above the monitor. Also, there needs to be a provision for a leak check adapter to be attached at the point where the PM <sub>10</sub> heads attaches if the downtube is not utilized.
Impactor	7.3.4	WINS with dimensions as described in Figures L-20 through L-24.	The WINS may be used or alternatively the Very Sharp Cut Cyclone (VSCC) or other cyclone providing an appropriate PM <sub>2.5</sub> separation may be used. The VSCC is expected to maintain an appropriate separation of coarse and fine particulate over a longer period of time than the WINS making it more suitable for use with PM <sub>2.5</sub> continuous monitors.
Filter Holder Assembly	7.3.5	Many specifications as described in the text and with dimensions as detailed in Figures L-25 through L-29.	Most of the filter holder assembly design specifications will not be applicable to PM continuous monitors. Some of the important areas to strive for in the design of a PM continuous method include: - providing for a uniform face velocity of the sample stream during sample collection preclude significant exposure of the filter (or surrogate collection device) to possible contamination.
Flow Rate Measurement Adapter	7.3.6	As described with the dimensions in Figure L-30	Ideally, this would be the same so that flow rate adapters would be interchangeable between FRMs and continuous methods.

Surface Finish	7.3.7	Anodized aluminum for all internal surfaces exposed to sample air prior to the filter.	Ideally continuous methods will also have anodized aluminum for all internal surfaces exposed to sample air prior to the filter or surrogate collection device. This is especially important to note for cyclones; if used, since they are not part of the FRM.
Sampling Height	7.3.8	2 meters $\pm$ 0.2 meters	Ideally, the sample inlet on a continuous method would meet this.

# **Performance Specifications**

Performance specifications for the FRM are largely associated with maintaining the flow rate within an acceptable range and the operational conditions for which the instrument should be capable of operating in. Most of the flow rate performance specifications for the FRM should be applicable to continuous methods; however, the operational conditions for which an instrument should be capable of operating in may or may not be applicable to any one continuous method. Many of these performance criteria can be applied to a potential continuous method. Most of the commercial vendors of PM continuous methods have already incorporated these performance criteria into their instruments. The table below describes the various performance specifications for the FRM and their applicability to PM continuous methods. Also, where appropriate, alternatives to the FRM performance specifications are offered:

Performance Specification Area	Section of Appendix L	FRM specification	Applicability to Continuous Methods
Sample Flow Rate	7.4.1	16.67 L/min measured as actual volumetric flow rate at the temperature and pressure of the sample air entering the inlet.	Generally applicable with the exception of any potential use of nephelometers. This flow rate is necessary if a PM <sub>10</sub> size selective inlet is used as well as for most second stage separators.
Leak Test Capability	7.4.6	Provide for an convenient external leak test capability	Generally applicable.
Range of Operational Conditions	7.4.7	Ambient Temperature - 30 to +45 C Ambient Relative Humidity 0 to 100 percent Barometric Pressure 600 to 800 mm Hg	Generally applicable as a starting point for design of an instrument; however, some continuous instruments may need to be located in an environmentally controlled shelter in order to have operate correctly. Some instruments may not meet all of these specifications which may limit their use geographically.
Ambient Temperature and Barometric Pressure Sensors:	7.4.8 and 7.4.9	Capable of operating over the range of operating conditions	Applicable for the operation of the continuous instruments in the range of environmental conditions they will encounter.
Filter Temperature Control	7.4.10	The sampler shall provide a means to limit the temperature rise of the sample filter from isolation and other sources to no more than 5C above the temperature of the ambient air surrounding the sampler.	It is desirable to minimize the temperature difference between the ambient air and the location where sample are collected and analyzed in a continuous method to provide for minimal volatilization of PM; however, in some cases heating may be necessary due to moisture interference or other reasons. Each potential continuous method should be designed to optimize this temperature difference with respect to avoiding moisture interference, PM volatilization, and stable measurement readings.

Filter Temperature Sensor	7.4.11	Capable of operating over the range of operating conditions	Generally applicable. However, may not always be necessary depending on the measurement principle of the continuous method.
Clock/timer system	7.4.12	Capable of maintaining local time and date including year, month, day of month, hour, minute, and second to an accuracy of ± 1.0 minute per month.	Generally applicable.
Outdoor Environmental Enclosure	7.4.14	Suitable to protect the instrument	Generally applicable for those instruments intended to be located outside. Not necessarily applicable to those instruments intended to be located in a station trailer or other environmentally controlled housing
Electrical Power Supply	7.4.15	105 to 125 volts AC (RMS) at a frequency of 59 to 61 Hz.	Generally applicable.
Data Output Port Requirements	7.4.17	Standard RS-232C	The Standard RS-232C data output connection can be utilized. Additionally, it is strongly encouraged to have a provision for an analog output that can be conveniently connected to a typical data logger utilized by ambient air monitoring agencies. For example, 0 - 10mV, 0-100mV, 0-1V, 0-5V, or 0-10V.

# Section 10. Linkage to national monitoring strategy

The EPA in partnership with it's principal grantees; States, Local agencies and Tribes, are formulating a national air monitoring strategy that strives to enhance the overall effectiveness of major regulatory based monitoring efforts throughout the nation. The continuous PM monitoring plan addressed here is a major part of that strategy.

The monitoring strategy provides a future direction for air quality networks throughout the United States. This direction incorporates knowledge acquired in air quality research and management practices over the last two decades, and takes advantage of the existing infrastructure of operating networks and monitoring agencies. The experience over the last 20 years suggests three basic enhancements in national network design:

- 1) **Promote multiple and collocated pollutant measurements** to improve how we diagnose cause effect phenomena in health effects and air pollution studies.
- 2) *Improve regional scale air quality characterization* to understand the linkage between background and transport concentrations (regional, continental, global scales) as they impact both rural and urban environments, an increasingly important need as the separation between rural and urban air pollution levels continues to decrease.
- 3) *accommodating new technologies* to provide timely reporting of air quality information to the public and to improve basic characterization of physical, chemical, temporal and spatial composition of air quality.

Consistent with these enhancements, the strategy has identified needed improvements to the monitoring program:

- characterization of hazardous air pollutants (HAPs);
- continuous particulate matter monitoring;
- information transfer and delivery;
- integration across pollutant programs; and
- optimization of the existing criteria pollutant monitoring networks.

This continuous monitoring implementation plan details EPA's proposal to optimize the PM components of the monitoring network. The broader vision for a PM network would use more continuous operating samplers and fewer filter-based samplers than the current system. The current PM<sub>2.5</sub> network of approximately 1100 integrated samplers (FRMs) and 200+ continuous samplers should evolve into a system of perhaps 700- 1000 PM<sub>2.5</sub> samplers with a more even distribution (e.g., 50-50) of integrated and continuous methods. The continuous methods must be integrated to ensure data compatibility with the current FRM network. The challenge in this strategy is to maximize the benefit of continuous samplers by allowing continuous monitors to be used for many applications including regulatory use.

#### Section 11. Regulatory Changes and Schedule

There are a number of federal regulations that are used to provide the framework for ambient air quality monitoring. These regulations cover the sampling and analytical methods used, how new methods are approved, quality assurance and control procedures, and basic monitoring objectives for certain air pollutants. Technical information is provided in guidance documents and through the Internet.

## **Specific Regulations to be Reviewed:**

There are three main regulatory "Parts" of the Code of Federal Regulations (CFR) that we intend to modify. These regulations are all part of CFR Title 40 which deals with the environment. Specifically:

40 CFR 50<sup>11</sup> Appendices: National Primary and Secondary Ambient Air Quality Standards (NAAQS), Appendix L. This regulation provides us with the NAAQS and the federal reference methods for measuring each air pollutant with an established standard. We are NOT going to modify the national ambient air quality standards with this regulatory review. Reviews and, if needed, revisions of the NAAQS occur in separate formal processes. We do want to review a portion of the minor requirements in the Appendix L portion of this regulation which describes the reference method for measuring PM<sub>2.5</sub>. The overall reference method will not be modified; however, we do want to examine some of the requirements for reporting supplementary data on the samplers' performance. We have successfully completed two annual quality assurance reports on the PM<sub>2.5</sub> FRM network operation, and we believe that we can reduce the amount of supplementary data being reported to EPA, specifically in Table L-1. This is a small change; however, it may provide some relief to State, local, tribal, and other monitoring agencies' data managers.

40 CFR 53 Ambient Air Monitoring Reference and Equivalent Methods. This regulation provides air quality monitoring instrument manufacturers with the application and testing requirements for reference and equivalent methods that must be followed in order to have their sampler/analyzer approved for regulatory use. The EPA's Office of Research and Development (ORD) is currently responsible for these approvals. This regulation describes the complexities of how new criteria pollutant methods can be formally introduced into the ambient air monitoring network. EPA is a strong proponent of this formal process given the policy and financial impact that decisions using data from federal reference and equivalent methods can carry. We will review this regulation; however, changes to it may or may not be taken in this package. The particulate matter National Ambient Air Quality Standard is being reviewed separately by the EPA. This separate process will also be used to promote continuous particulate matter monitoring technologies within our regulations.

The EPA's ORD has established a Reference and Equivalent Method Board that includes members from OAOPS and ORD. This Board's function has been to review new and modified proposals for fine particulate matter monitoring candidate methods, and to provide broader program input into the approval process. OAQPS proposes to expand the

<sup>&</sup>lt;sup>11</sup>Regulations are cited in documents using the format "Title# CFR Part#".

role for this Board to include identifying how to incorporate regional equivalency into the existing reference and equivalent method testing program prior to any actual regulatory change. This approach may need to take the form of a pilot project initially. We will also need to examine our regulatory authority for making such a change. There is a precedent for approving regionally based equivalency within the particulate matter program, specifically with the approval of the Oregon DEQ Med-Vol sampler. It will be necessary to follow-up with any regional equivalency process with formal regulatory changes to Part 53.

**40 CFR 58 Ambient Air Quality Surveillance.** This regulation is a primary focus of our efforts to both incorporate new technologies and to provide data as outlined in the national monitoring strategy. Nearly all data collection and reporting requirements, all the quality assurance requirements, the NAAQS pollutant network design criteria, the air quality index reporting, and annual data certification requirements are included within this regulation. This regulation describes how the Clean Air Act air monitoring authority has been interpreted and implemented by the EPA and our State and local agency partners for air pollutants with established NAAQS. Tribal agencies are not regulated under this provision; however, the technical requirements within should be familiar to any tribal agency that plans to conduct monitoring.

We expect to change the 40 CFR 58 regulations to allow more flexibility in designing the particulate matter monitoring network. One of these changes would include modifying the existing correlated acceptable continuous (CAC) particulate matter monitoring approach to allow for a more network-based approach rather than only the site-by-site approach as defined currently. The original CAC provisions were developed prior to the full deployment of sequential federal reference methods (FRMs) for fine particles as a way to provide sampling frequency relief from daily sampling. Since the sequential FRMs have been available and are working, the CAC provision has largely been ignored by air monitoring agencies. EPA will modify this provision so that it will provide a better mechanism for incorporating continuous particle monitors into the network.

## **Participants in the Regulatory Review**

We have solicited input from a variety of parties for this regulatory review process. Through the larger air monitoring strategy, we have created a National Monitoring Strategy Committee that is providing advice and recommendations for the national air monitoring program. Some of these recommendations will be realized only after regulatory change has taken place. The NMSC has been discussed in section 10 of this document.

We have also created three separate work groups, one each for the subjects of regulatory review, quality assurance, and technology. These work groups were established to make some concrete progress on the program changes needed to realize the national monitoring strategy goals. The quality assurance group will provide recommendations for changes to the quality assurance provisions of the monitoring regulations as well as all existing quality assurance practices; and the technology work group will make recommendations for use in the methods sections of the regulations and in technical guidance used by monitoring agencies. The regulatory review work group must take information from all of these parties, in addition to the NMSC and the work group's own recommendations, and develop an appropriate regulatory package.

The NMSC and the three work groups include representatives from the EPA OAQPS, the

ten EPA Regional Offices, State agencies, local agencies, and tribal governments. All regulatory changes will undergo public review and comment inherent within the regulatory modification process. EPA will also work through existing mechanisms such as the STAPPA/ALAPCO Monitoring Committee and the Standing Air Monitoring Work Group (SAMWG) to communicate with stakeholders on these regulatory changes.

#### Schedule

The National air Monitoring Strategy identifies the need to review and revise the federal monitoring regulations in order to create an air monitoring system that is responsive to current and emerging environmental data needs. Along with a variety of topics, we intend to review and modify these regulations to incorporate more continuous particle techniques. The proposed monitoring strategy regulatory changes are being incorporated into the PM NAAQS review and this schedule reflects this merging of rule-making actions.

Key Milestones (later milestones are subject to change):
October - NMSC recommendations on the national network.
October 23-25, 2001 - Monitoring Strategy Workshop
December 2002 - Draft rule-making language prepared for work group review.
June 2003 - Proposal in the Federal Register
July-September 2003 - Public comment period
October - December 2003 - Review public comments, prepare responses
January 2004 - Final regulatory package published in Federal Register

# Section 12. Summary of Issues and Action Items

This document serves as a bridge between concepts for integrating continuous PM monitors presented at meetings with the Clean Air Science Advisory Committee's Subcommittee on Particle Monitoring in January, 2001 and January, 2002 and comprehensive guidance for monitoring agencies. There remain numerous details not addressed at this time that should be addressed to ensure a satisfactory outcome. These issues and other areas of concern include:

- Complex program. The concepts and elements incorporated in this plan are singularly and collectively complex therefore creating a communications challenge. Other approaches were considered, but the potential drawbacks of a simplistic approach were not acceptable. That is, it would have been easy to develop a rigorous non-flexible program easily communicable but conveying little motivation for deployment. Similarly, a program without constraints would likely compromise data quality and interpretability. Thus, a decision was made to accommodate both flexibility and data comparability at the expense of developing and communicating a complex program.
- Rescinding REM certification based on future poor performance. The REM program is based on demonstrating an acceptable level of comparison between FRM and continuous samplers. This relationship may change as a result of atmospheric changes due to deployment of emission mitigation strategies. Guidance, albeit complex, will allow for a non static relationship. Nonetheless, this potential for aerosol change will require iterative evaluation of instrument performance that is likely, in some instances, to show that a previously approved REM fails performance goals.
- C Developing and approving regional equivalent domains. The information in this document can be applied in a somewhat straightforward manner for approving an instrument for CAC or REM purposes at an individual site. The larger goal is to broaden this acceptance to a "region" where the meteorological and aerosol composition characteristics exhibit consistent behavior and hence throughout which the continuous and FRM methods exhibit similar relationships. Regionality is further complicated by administrative and demographic issues (e.g., multiple monitoring agencies and State boundaries intersecting within a given "region"). To simplify implementation, the proposal in this document is to start with approval across an entire State. Multiple States may seek approval in a coordinated effort or a State may need to be broken down into smaller sub-domains. Geo-political boundaries can have the have the advantage of a consistently implemented monitoring program (One state monitoring agency having oversight for all monitoring operations within that state); however, regions of performance are more likely associated with the homogeneity of the aerosol encountered. This may be larger or smaller than the domain of a state.
- Reliance on FRM measurements as an indicator. The underlying approaches require comparability of continuous and FRM measurements. The reason for this is that so many objectives relate to the FRM measurement (e.g., NAAQS comparisons, AQI, air quality model application). In many instances, there is no technical reason to expect comparability between disparate measurement approaches. Such comparability is desired given the utility of relating continuous measurements to a wealth of existing FRM data and to incorporate a reference marker. The downside of this approach is that the value of an

FRM measurement is assumed or inferred to be greater than that of a candidate method, when in some cases the candidate method may better reflect "true" characteristics of an aerosol.

- Specific Guidance on Performance Specifications. Sections 5 8 introduce performance specifications for bias, precision, and correlation but several specific details are not addressed. For example, how is bias measured? What is the statistic as well as what is the source of the data to be used in the statistic? Are bias estimates based only on existing collocated instruments or is an independent audit required? How are bias and precision treated on a regional basis, does the failure of one site constitute failure for a region, or are all estimates averaged across a region? What is the appropriate frequency for checking bias and precision? These unique considerations warrant development of a dedicated Quality Assurance program for CAC and REM applications.
- Integrating Correlation with the PM2.5 DQOs. Section 6 presented an initial attempt to identify correlation criteria for CAC and REM. The basis for the correlation criteria presented includes: evaluation of the existing network; expected sample size for a years worth of data at a routine site; identification of a desired *true* underlying correlation, and selection of tolerable error rates. At this time it is not known how integrating a correlation criteria would affect the PM2.5 DQO's. More work will need to be performed to integrate correlation with the PM2.5 DQO's.
- C Data interpretation and management. Transformed data are to be submitted to AIRS. How do analysts gain access to raw non-transformed data? Transformation models are based on 24-hr comparisons, yet transformed data will be reported continuously, which may create odd results in discrete hourly reporting. Coding specifications for CAC and REM need to be developed.
- Demonstration of performance. The bias and precision estimates are based on existing network performance. This implies that the testing to meet such specifications should be conducted under conditions consistent with routine operations. This approach should not be interpreted as excluding desired vendor participation. Responsibilities for conducting testing, developing transformations and communicating performance results requires further effort.
- Consistency with FEM. The current Class III equivalency requirements appear to be more strict than what a FRM can meet. That is, the imprecision in the FRM is such that the correlation requirement can not be met, not because of the challenging instrument, but because of the instrument being used as the standard. This inconsistency needs to be addressed. In doing so, it may make it possible for an instrument to acquire a Class III equivalency. Work will be initiated to evaluate the necessary performance criteria for national Federal Equivalency based upon a DQO approach.

## **Section 7.** Monitoring Methods and Issues

#### 7.1 Background/Introduction

The Strategy goal is to manage the Nation's air monitoring networks such that critical and stable network elements, as well as changing priorities, can be accommodated in a framework that is scientifically sound and resource-optimized to address national and local interests. This framework requires progress on various aspects that shape the monitoring networks, including the incorporation of emerging technological and scientific advances in measurement techniques to support these monitoring efforts. Several different measurement techniques are needed to support the existing monitoring program efforts. The list of measurements provided in Section 4 includes mostly those that are required with some recommendation on additional measurements.

The information in this section supports the overall Strategy approach by providing a general understanding of (and issues related to) routine monitoring and new technologies currently available to provide the measurements outlined in the Strategy. Its goal is to help provide insight for those deciding how these measurements will be obtained. An attempt is made to strike a balance between the routine, easy-to-use, "tried and true" and the new, commercially available, continuous, and not-yet-fully-demonstrated technologies. Recognizing that other techniques may be applicable to the measurements discussed, the methods provided here are those used in current EPA monitoring networks. This discussion does not include PM mass and PM continuous measurements.

It is important to distinguish between "routine" and "non-routine" methods for monitoring. Routine methods are thought to be fully field demonstrated, tested and routinely used in networks such as the National Ambient Air Quality Standard (NAAQS) networks. Routine methods are those that are usually simple to implement, use and maintain, stable in operation and do not require significant resources to operate. Non-routine methods are considered less "rote," more research-oriented, more difficult to maintain, and require a specially trained or skilled operator. Non-routine methods may also be new technologies that have not yet been fully field tested or evaluated.

In keeping with the goal of providing insight to those implementing monitoring methods, this section is an overview of the methodologies, and a synopsis, of what is considered to be currently "working" and what is not. This section touches on the key issues with each of the methods and is grouped by program. It is not in any order of priority. To address an overview of measurement method operating principles for gasphase species that are relevant to secondary PM formation, refer to **Attachment 7.1** as excerpted from Seigneur et. al., 1998. The overview of operating principles for the remaining species is included here.

#### 7.2 Criteria Pollutants (CO, SO<sub>2</sub>, NO<sub>2</sub>, O<sub>3</sub>)

Federal Reference Methods (FRMs) and Equivalent Methods (FEMs) used for criteria pollutants were developed by the Office of Research and Development (ORD) and are explicitly defined in the Federal Register. The methods for the criteria pollutants (except PM and lead are not addressed here) are working well for NAAQS decision-making purposes. In considering these methods for other applications, such as measurements in rural areas or for more research-oriented applications, technical issues and limitations have been identified. In addition, as these methods have been implemented and operated under rigorous field conditions, over time issues have been uncovered. In some cases, the issues are inherent limitations in the technique being applied and in other cases the issues are difficult to resolve because they are not reproducible.

When applied to situations where very low concentrations need to be measured (e.g., rural monitoring), issues with measurement sensitivity exist for the CO and SO<sub>2</sub> methods. Manufacturers of NDIR (non-dispersive infrared) CO monitors are continuing to improve the performance and offering "high-sensitivity" options, like the TECO 48C trace-level analyzer, that allow for detection limits around 0.10 ppbv. The principal constraints on the ability to lower detection limits further are detector noise, interference from water vapor and background drift. These issues can be addressed by drying the sample stream, frequent zero and span checks (e.g., every 90 seconds), and active temperature control of the optical bench and instrument cabinet. This requires a significant amount of post-data processing that may be burdensome for some.

Similar issues with sensitivity for rural or background applications apply to automated methods for  $SO_2$ . High-sensitivity options of the pulsed-UV fluorescence continuous monitoring technique (e.g., TECO 43C trace-level analyzer) provide lower detection limits on the order of 0.10 ppb for 60 second averaging times.  $SO_2$  monitors are affected by temperature and water vapor. The temperature affect is not as great as with CO monitors; therefore, no on-board temperature control is necessary. These limitations can be addressed by frequent zero and span checks. A NOx interference exists. There is a NOx rejection ratio of 40-50:1, where 40-50 ppb NOx results in a 1 ppb SO2 instrument response.

Oxides of nitrogen, NO<sub>x</sub> (NO<sub>2</sub> + NO) measurements using chemiluminescence do not determine NO<sub>2</sub> directly. NO is determined directly and NO<sub>2</sub> is determined by the difference between the measured total NO<sub>x</sub> value and the corresponding measured NO. Chemical reductant and heated metal converters are not specific for NO<sub>2</sub> and convert all nitrogen species present in the atmosphere to NO. This presents a positive bias in the measurement of NOx and consequently NO<sub>2</sub>. As such, these instruments serve as better NO<sub>y</sub> monitoring devices in rural areas than NO<sub>2</sub> monitoring devices because of the non-specific conversion of nitrogen species. Sensitivity of the instruments is adequate (as low as 2 ppbv) for rural applications, but a "direct or true" NO<sub>2</sub> measurement is needed. A photolytic converter can provide improved accuracy in determining both NOx and NO<sub>2</sub>. EPA-ORD is currently evaluating instruments that can be used in conjunction with

the current NO<sub>x</sub> monitors and complete stand-alone photolytic systems. Photolytic system detection limits are on the order of 3 ppt. Diode lasers now available in photolytic converters are another alternative being evaluated by ORD.

Measuring NO<sub>v</sub> is a valuable adjunct to NO and NO<sub>x</sub> monitoring because the individual species comprising NO<sub>v</sub> include not only NO and NO<sub>2</sub>, but also other organic and inorganic nitrogen oxide compounds that constitute a more complete measure of nitrogen oxides emissions. In typical urban environments, the principal NO<sub>v</sub> compounds are NO, NO<sub>2</sub>, HNO<sub>3</sub>, and PAN. Determining NO<sub>v</sub> concentrations is useful in establishing nitrogen oxide emission patterns and temporal trends, and in assessing the photochemical "age" and reactivity of air masses. Guidance on measuring NO<sub>v</sub>, including measurement principles, calibration procedures, and equipment descriptions, have been prepared for the PAMS program. It is not possible to individually measure all the compounds that comprise ambient NO<sub>v</sub>. Measuring several key NO<sub>v</sub> constituents is expensive and technically difficult. However, the chemiluminescence monitoring approach for NO and NO<sub>x</sub> described above is a practical approach to determining the total NO<sub>v</sub> level, once the converter has been moved as close to the inlet as possible. For consistency in measurements, NO<sub>v</sub> should be measured in a practical and standardized manner. Instruments used to measure NO<sub>v</sub> should be sensitive enough to measure the low concentrations typically encountered during the late afternoon as well as the high concentrations encountered during the early morning hours of the day. Automatic measurement range changing will more reliably accommodate the range of NO<sub>v</sub> concentrations experienced in a typical urban atmosphere. It is recognized that NO<sub>v</sub> measurement is an emerging technology and as advances in the technology are made, the methods should be updated.

Chemiluminescence is the FRM for ozone; however, the most popular technique for ozone has been UV photometry because of simplicity and ease of use. UV ozone monitors are susceptible to interferences by aromatic hydrocarbons, water vapor and mercury. Whether water vapor truly presents an interference is still under debate. Erratic readings and sometimes cycling monitor baseline readings have been identified by a few state agencies, but the cause of these anomalies has yet to be reproduced or positively identified. Theories have revolved around the specific type of ozone scrubbing device used in the monitor (MgO) and proper scrubber performance is critical to minimizing interferences. Where high levels of potential interferences are expected, the use of chemiluminescence monitors are recommended; however, commercial availability of these monitors is limited.

#### 7.3 PM<sub>2.5</sub> Chemical Speciation

The most challenging measurement component in the speciation program is carbon, for both the carbonaceaous aerosols (organic and elemental carbon) and semi-volatile organic aerosols or organic PM. The analysis of organic (OC) and elemental carbon (EC) is operationally-based and dependent on the purpose of measurement and the specific analytical technique used. Currently, there are no reference standards for

carbon or a standardized method for distinguishing between organic and elemental carbon; therefore, differing results are obtained for the same sample depending on the analytical method operating parameters used. The sampling of carbon is not without issue. Positive and negative sampling artifacts complicate sampling and add a large degree of variability and uncertainty into the measurement. The issues on artifacts are captured in the discussion of organic PM below.

Due to the number of organic compounds present, characterization analysis of the organic chemical composition of PM<sub>2.5</sub> presents a difficult challenge. The collection of particulate organic matter can be accomplished using particulate sampling instruments equipped with quartz fiber or Teflon®-impregnated glass fiber filters and denuders. This methodology is susceptible to negative (i.e., desorption of semi-volatile compounds from the particles on the filters) and positive (i.e., adsorption of gases by the filter material and particles collected) artifacts. Positive and negative artifacts are of most concern, but there is disagreement as to the cause and extent to which they bias organic PM measurements. The positive artifact is currently thought to be the largest of the two artifacts. The use of denuders is controversial. Stripping of gases upstream of the sampling filter by denuders may disturb the gas-particle equilibrium of the organics, providing a driving force for volatilization. Thus, volatile losses from a filter downstream of a denuder may be greater than the volatile losses experienced by an undenuded filter. Research continues on the development of a denuder that has adequate efficiency and is practical to use.

Once collected, characterization analysis of organic chemical composition requires the analysis of numerous calibration standard mixtures. This is needed to cover the range of compounds that may be of interest as a result of the hundreds of organic compounds associated with both the gas and particle phases in the atmosphere. The availability and cost of acquiring and synthesizing these analytical standards is problematic.

X-ray fluorescence (XRF) is currently used to obtain data for elemental composition of PM<sub>2.5</sub>. There are limitations of XRF for the determination of beryllium and the sensitivity of the method (e.g., detection limits) for certain applications. If the application requires quantification of beryllium or greater sensitivity, then consideration should be given to the use of ICP-MS (i.e., inductively coupled plasma - mass spectrometry) as a viable alternative. Comparisons of data obtained by both XRF and ICP-MS have shown the sensitivity of ICP-MS to be an improvement over XRF for some elements. However, ICP-MS is not a panacea. There are some cases where sensitivity of ICP-MS is not as good as XRF (e.g., calcium and potassium). Clearly, more comparison work on PM<sub>2.5</sub> samples is needed to determine the benefits of XRF and ICP-MS. XRF is non-destructive and typically places the filters under vacuum which may cause volatile compounds to evaporate. As a result, species that can volatilize, such as ammonium nitrate and certain organic compounds, can be lost during the analysis. The effects of this volatilization are important if the filter is to be subjected to subsequent analyses of volatile species. In the PM<sub>2.5</sub> speciation program, the XRF filter is not used to quantify

volatile species. ICP-MS is a destructive technique and once filters are subject to analysis no repeat analyses can occur.

#### 7.4 Continuous PM<sub>2.5</sub> Speciation Instruments

Commercial instruments are currently available to measure carbon (OC, EC, TC), nitrate and sulfate. These instruments provide time-resolved measurements from a few minutes to a few hours. They have been field tested and inter-compared through the ETV (Environmental Testing and Verification) program and the Supersites program, and considered to be good candidates for additional testing. Very limited data are available to completely understand the comparison with filter-based methods and the inherent limitations of these technologies. More comparison data are available for the carbon instruments (Aethalometer and R&P5400) as opposed to the nitrate and sulfate instruments. Good correlation with filter-based methods has been found for the R&P5400, but the measurement is biased low. Nitrate, sulfate and carbon continuous instruments will be tested through the EPA's speciation program where they will be run in conjunction with the standard filter-based methods.

The aethalometer has undergone much more extensive inter-comparison testing and has shown very good correlation of BC with EC in a number of studies. Agreement with filter-based methods is highly variable across studies and may be due to the specific attenuation used by the instrument to determine BC. This value can be modified by the user. The aethalometer requires very little maintenance, has on-board data acquisition and can perform for long periods of time without operator involvement.

A continuous PAH (polycyclic aromatic hydrocarbon) monitor is available (EcoChem PAS 2000). Very limited inter-comparison data were collected through ETV due to the very low concentrations of ambient PAH during the test period. The monitor was rated very easy to operate and provides a total PAH measurement only. It is somewhat sensitive to temperature, and requires a "shield" from sunlight. Clearly more field and comparison testing is needed.

#### 7.5 Hazardous Air Pollutants (HAPs) or Toxics

Standardized methods for HAPs are being used in the EPA's Urban Air Toxics Monitoring Program (UATMP) and Air Toxics Pilot Monitoring Network. Most of these methods for VOCs, metals, and carbonyls are adequate for the data collection needs; however, due to the push to leverage existing methods to cover as many of the key HAPs as possible, there are some that cannot be covered by the existing methods used for these programs. Examples include acrolein and ethylene oxide. There are methods for these compounds, but it would require added burden be placed on state agencies to add two more methods to the suite they already have. There are also a few HAPs for which no methods are available (e.g., hydrazine and quinoline). Acrolein is considered a critical HAP from the standpoint of risk, and is not stable using dinitrophenylhydrazine (DNPH)-coated cartridges and Method TO-11a. Because of its importance, ORD, consultants, and some state agencies have done some work to develop methods for acrolein. This work

includes the possible use of Method TO-15 for VOCs and stainless steel canisters; modification of the existing DNPH Method TO-11a; and a method that uses dansylhydrazine-coated C18 cartridges (developed at Rutgers). In addition to total chromium measurements, chromium species (e.g., Cr III and Cr VI) are of interest. CARB has developed a method for Cr VI that has been used by the EPA in emergency response applications. A modification of the CARB method is currently being used by the EPA contractor for the UATM program.

As data from the pilot monitoring network is analyzed, the need for enhanced method sensitivity to meet risk-based concentration requirements may be needed. Sensitivity of the standard methods for one-in-a-million risk-based concentrations would require additional method development for many of the target compounds, especially the chlorinated VOCs. This issue will need to be further evaluated as the pilot network data are analyzed and the program DQOs are developed.

Automated and continuous instruments are commercially available for formaldehyde and speciated gas-phase mercury. Continuous formaldehyde instruments have recently become commercially available in the U.S. at a cost of about \$27K (e.g., Alpha-Omega PT). There is also at least one other vendor of instruments of a similar type in Germany (Aero Laser), and the cost is about \$38K. The U.S. monitor uses a wet chemical technique that poses some issues with operation and maintenance. Regular maintenance includes filling the liquid reservoirs and replacing pump tubing weekly. The monitor is also susceptible to formation of leaks and bubbles which interfere with data collection. The monitor requires a substantial supply of zero air and is most practically supported by a zero air compressor system or zero air generator. Gas calibration can be done using either a gas cylinder of formaldehyde or a permeation tube device. Liquid calibration can also be done using solutions of formaldehyde; however, liquid calibration does not check the inlet and the formaldehyde-scrubbing device. Intercomparison testing of a prototype monitor during the 1999 Nashville SOS showed good comparison (14 % difference) with a Tunable Diode Laser Absorption Spectrometer (TDLAS) when analyzing a formaldehyde audit cylinder. These monitors require more testing in routine field applications by state agencies to get a better feel for complexity of operation and data recovery. The units are very promising, but somewhat complex to operate and maintain.

A continuous mercury monitor is available (Tekran) that provides both total mercury and speciated or reactive gaseous mercury (RGM) measurements. This instrument has been used extensively by ORD in Florida and other parts of the country. It is recommended that particulate mercury be collected in conjunction with gaseous elemental and RGM to provide a complete picture of the atmospheric behavior of mercury for modeling and emission inventories purposes. Continuous mercury monitors for total and RGM are expensive (~\$95K). An RGM artifact formation on quartz filters collected for particulate mercury has been identified which is resolved through the use of the KCl- coated annular denuder before the quartz filter.

# **Attachment 7.1**

**Measurement Methods** 



# GUIDANCE FOR THE PERFORMANCE EVALUATION OF THREE-DIMENSIONAL AIR QUALITY MODELING SYSTEMS FOR PARTICULATE MATTER AND VISIBILITY

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#### A.1 Measurements of Precursor and Oxidant Gases

This appendix describes measurement methods for gas-phase species that are relevant to secondary PM formation, either directly as precursor species (e.g., NO, NO<sub>2</sub>, HNO<sub>3</sub>, NH<sub>3</sub>), or as gas-phase species that act as oxidants in air, for example those that oxidize NO to NO<sub>2</sub> to HNO<sub>3</sub>. Several species partition between the gas and particle phases depending on, for example, temperature and relative humidity. For these species, measurements that strictly measure the gas-phase components, typically continuously, are described in this section. Methods that can simultaneously measure the gas and PM components are described in Section A.2 These methods typically are time-integrated measurements over a few hours to a full day.

Table A-1 summarizes the principal methods used to measure precursor and oxidant gases. The measurement methods are described below by chemical or group of chemicals.

## **A.1.1** Nitrogen-Containing Species

Methods for the measurement of gas-phase nitrogen species have been reviewed recently by Solomon (1994a) and Parrish and Fehsenfeld (1998). Species included in the reviews are nitric oxide (NO), nitrogen dioxide (NO<sub>2</sub>), peroxyacetyl nitrate (PAN), other peroxy nitrates, organic nitrates, nitrate radical (NO<sub>3</sub>), nitric acid (HNO<sub>3</sub>), and total reactive nitrogen oxides (NO<sub>y</sub>). The two reviews differed in their approach. Solomon (1994a) reviewed methods available in 1990 for the purpose of recommending methods for use in the 1990 San Joaquin Valley Air Quality Study (SJVAQS) field program. Thus, Solomon attempted to provide practical information for decisions regarding which instrument to use in the field, stressing analytical capabilities and pros and cons of the methods, including, for example, cost, reliability in the field, and availability. Discussions also included examining results from methods comparison studies for measurements at the surface and aloft. It was updated prior to publication in 1994. Parrish and Fehsenfeld (1998) performed a critical review of current methods, stressing mostly recent developments and methods suitable at very low concentrations, and

Table A-1. Measurements of Precursor and Oxidant Gases

Method	Variable Measured	Limit of Detection (3σ)/Avg. Time	Precision (1σ)	Overall Accuracy	Potential Interferences/Artifacts	References
Chemiluminescence						
With O <sub>3</sub> to NO <sub>2</sub> *	NO	15 pptv/1s	5%	<u>+</u> 15%		Fahey et al., 1986
Photolysis to NO	NO <sub>2</sub>	30 pptv/1s	5%	<u>+</u> 30%	Conversion of NO <sub>y</sub>	"
Reduction to NO	$NO_y$	60 pptv/1s	5%	<u>+</u> 15%	NH <sub>3</sub> , HCN	"
Luminol	NO <sub>2</sub>	100 pptv/30s	5%	<u>+</u> 10%	O <sub>3</sub> , PAN	Fehsenfeld et al., 1990
with NO to NO <sub>2</sub> *	$O_3$					Parrish et al., 1998
with ethylene	$O_3$				water vapor	"
Eosin-Y	$O_3$	1 ppbv/4s	0.8 ppb at 0 ppbv O <sub>3</sub>		SO <sub>2</sub> (8% at 300 ppbv SO <sub>2</sub> )	Topham et al., 1990; Topham et al., 1992
Chemical Amplifier	HO <sub>2</sub> , RO <sub>2</sub>	6 pptv/1m		<u>+</u> 100%	PAN, PNA, H <sub>2</sub> O <sub>2</sub> , O <sub>3</sub> , variable chain length	Cantrell et al., 1993 Hastie et al., 1991
Gas Chromatography – FID or Mass Spectroscopy	VOC	10 pptv/45m	3% @1ppb	<u>+</u> 18%		Goldstein et al., 1996
NSIS or TDLAS	СО	1 ppm, 0.25 ppb	10%, 4%			Fried et al., 1991
Gas Chromatography – Luminol	PAN	25 pptv/30 m		<u>+</u> 25%		Blanchard et al., 1990
GC-FID, GC-MS	alkyl nitrates					
Chemical Ionization Mass Spectrometry	ОН				inlet surface loss	Tanner et al., 1997
	HNO <sub>3</sub>	13 pptv/1s	10%	<u>+</u> 35%	reactor surface effects	Huey et al., 1998
	HO <sub>2</sub> , RO <sub>2</sub>		20% @20 ppt	<u>+</u> 45%	calibration uncertainties	Reiner et al., 1997
Matrix isolation-ESR	HO <sub>2</sub> , RO <sub>2</sub> NO <sub>3</sub>	2 pptv				Mihelcic et al., 1993
		1 pptv				

Table A-1. Measurements of Precursor and Oxidant Gases (continued)

Method	Variable Measured	Limit of Detection (3σ)/Avg. Time	Precision (1σ)	Overall Accuracy	Potential Interferences/Artifacts	References
Differential optical absorption	NO <sub>3</sub>	2 ppt/10 m			water vapor	Carslaw et al., 1997
spectroscopy	$NO_2$	4 ppb/12 m		±15 %		Biermann et al., 1988
	HONO	ppb/12 m		±30 %		"
	ОН	0.02 ppt/2 m	1%@0.2 ppm	±25 %	none	Mount, 1992
	$SO_2$	20 ppt/10 m				Platt, 1994
	$\mathrm{CH_{2}O}$	400 ppt/10 m				"
	$O_3$	4 ppb/10 m				"
Fourier transform infrared spectroscopy	CH <sub>4</sub>	(ambient)/1 m	0.2% @2 ppm	±5 %	none	Galle et al., 1994
	HNO3	4 ppb/15 m		±10 %	none	Biermann et al., 1988
	VOC	1 to 100 ppb			spectral congestion	Hanst and Hanst, 1994
Tunable diode laser absorption	NO	1 ppb/1s	5%@10 ppb	±15%	optical fringes, thermal drifts, laser mode impurity, laser mode drifts	Pun, 1998
spectroscopy	$NO_2$	0.5 ppb/1s	5% @ 10 ppb	±15%		"
	$O_3$	2 ppb/1s	5% @ 10 ppb	±15%	inlet loss, surface memory	"
	$HNO_3$	240 ppt/10 m	10% @ 1ppb	±15%	none	Horii et al., 1997
	$\mathrm{CH_4}$	(ambient)/1s	0.1% @2 ppm	±5 %	uncertainty in data base	Zahniser et al., 1995
	$C_2H_6$	300 pptv/1s	10% @ 1ppb	±20%	none	Zahniser et al., 1998
	CH <sub>2</sub> O	100 ppt/5 m	5% @ 1ppb	±12%	none	Fried et al., 1997
	CO	(ambient)/5s	1% @ 50 ppb	±1%		Sachse et al., 1991
Non-dispersive infrared absorption	CO	(ambient)/1 h	2% @ 200ppb		water vapor on catalyst	Parrish et al., 1994
	$CO_2$	(ambient)/10 s	0.1%			

Table A-1. Measurements of Precursor and Oxidant Gases (continued)

Method	Variable Measured	Limit of Detection (3σ)/Avg. Time	Precision (1σ)	Overall Accuracy	Potential Interferences/Artifacts	References
Laser induced fluorescence	ОН	0.01 ppt/60s	5-15%	±16 %	sensitivity varies with H <sub>2</sub> O	Hofzumahaus, 1996
	$HO_2$	0.005 ppt/30s	30%	±50%	conversion to OH with NO	Stevens et al., 1994
	$NO_2$	280 ppt/2.5 m		±15 %	none at present	Fong et al., 1997
	NO	<5 ppt				Bradshaw et al., 1985
UV absorption	$O_3$	1 ppbv/ 10 s		±3 %	none	
VUV fluorescence	CO	2 ppbv/ 10 s				Haaks, 1998
TTFMS	NO	Low pptv range				Cooper et al., 1994
	$NO_2$					
	$HNO_3$					
	PAN					
	$H_2O_2$					

highlighting tests or comparison studies performed to determine instrument reliability. Both reviews provide brief descriptions of the methods. Much of the information described below is summarized from these reviews.

In this report, unless otherwise noted specifically,  $NO_x$  refers to the sum of  $NO + NO_2 + some$  typically unknown fraction of interfering species (i.e. other nitrogen oxides) rather than just the sum of  $NO + NO_2$ .  $NO_y$  refers to the true sum of all gas-phase reactive odd-nitrogen oxide species:  $NO + NO_2 + HNO_2 + NO_3 + PAN + NO_3 + HONO + 2N_2O_5 + aerosol nitrate + organic nitrates + etc. (Bollinger et al. 1983, Logan 1983, Dickerson 1985, Fahey et al. 1985, Fehsenfeld et al. 1987, Kelly et al. 1989). <math>N_2O_5$  is included in the list of odd-nitrogen species because it is in equilibrium with  $NO_2$  and  $NO_3$ .

#### Nitric Oxide (NO)

Several methods are available for the measurement of nitric oxide in the atmosphere. These include the widely used ozone (O<sub>3</sub>)/NO chemiluminescence method and four spectroscopic techniques: tunable diode laser absorption spectroscopy (TDLAS), differential optical absorption spectroscopy (DOAS), two-tone frequency modulated spectroscopy (TTFMS), and laser-induced fluorescence (LIF).

The O<sub>3</sub>/NO chemiluminescence method is widely used for the measurement of NO in the atmosphere. It is based on the chemical reaction of NO with added ozone followed by the detection of radiation emitted by an excited state of the NO<sub>2</sub> formed in the reaction of NO and O<sub>3</sub> (Fontjin et al., 1970; Ridley and Howlett, 1974). The intensity of the reaction is proportional to the concentration when properly calibrated against NO standards of known concentration. Background chemiluminescence, for example, from hydrocarbon species that chemiluminesce slower on reaction with O<sub>3</sub> than NO, can be minimized by the use of a pre-reaction chamber (Ridley and Howlett, 1974; Delany et al., 1982; Dickerson et al., 1984; Drummond et al., 1985; Grosjean and Harrison, 1985; Kley and McFarland, 1980; Kelly, 1986). The pre-reaction chamber also allows for the maintenance of a stable instrument zero if operating properly. Several of the commercially available instruments sold since the early 1990 include a pre-reaction

chamber (e.g., TEI Model 42S and Tecan Envia Model CLD 700 AL). Limits of detection range from about 5 ppb in older, pre 1990 units (e.g., TEI Model 14) to in the range of 0.5 - 1 ppb (e.g., TEI 42), to 0.01-0.50 ppt (e.g., TEI Model 42S). Accuracy and precision are well established for this method and when used in intensive monitoring networks are on the order of about 5-10% depending on the concentration range of interest (Solomon and Thuillier, 1994, p. 5-8 and references cited therein). The O<sub>3</sub>/NO chemiluminescence method has been compared to the two-photon LIF method under low NO concentrations. Agreement was within 15-20 ppt and an uncertainty of 5 ppt was noted in the measurement (Gregory et al., 1990a).

TDLAS relies on measuring the absorbance of IR radiation at specific wavelengths due to a single pollutant (Schiff et al., 1983, 1987; Walega et al., 1984; Mackay and Schiff, 1987; Finlayson-Pitts and Pitts, 1986 and references cited therein). A number of chemical species have been measured, including CO, O<sub>3</sub>, SO<sub>2</sub>, N<sub>2</sub>O, NH<sub>3</sub>, CH<sub>4</sub>, HCl, NO, NO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, HCHO, and HNO<sub>3</sub> (Mackay et al., 1988, 1990; Drummond et al., 1989a; Schiff et al., 1990; Fried et al., 1991; Pokrowsky and Herrmann, 1981). The detection limits for NO and other species is about 0.025-0.5 ppb and depends on factors such as integration time and path length that range from 0.1 to 1 km (Schiff et al., 1983; Mackay and Schiff, 1987; Mackay et al., 1988; Fehsenfeld et al., 1990). The TDLAS provides a nearly interference-free measurement of the specific species monitored (Schiff et al., 1983), and therefore, has been considered the reference method in a number of intercomparison studies (Hering et al., 1988; Drummond et al., 1989a; Sickles et al., 1990; Fehsenfeld et al., 1990; Gregory et al., 1990a). The TDLAS requires a skilled operator. Since the TDLAS can be considered a reference method, its use, at least at one site, is strongly recommended for quality assurance/quality control (QA/QC) purposes. However, caution is recommended as the sample is brought into the system through an inlet line and losses or chemical reactions can occur during transport through the inlet line.

DOAS determines atmospheric concentrations in situ by measuring the absorption of the species of interest in the ultraviolet/visible wavelength region. DOAS is based on measuring the difference between the absorbance at a wavelength where the species of interest has a distinct peak, and another wavelength on either side of that peak (Platt et

al., 1980; Winer and Biermann, 1989 and references cited therein; Biermann et al., 1988; Finlayson-Pitts and Pitts, 1986 and references cited therein; Plane and Nien, 1992; Plane and Smith, 1995). High sensitivities are obtained by combining the detector with a long-pathlength, using either natural light (the moon or near-dawn sunlight) or a multiple-reflectance system, the latter of which yields optical pathlengths up to 10 km (Plane and Smith, 1995; Smith et al., 1995; Solomon et al., 1989a, 1989b). Concentrations are determined from the pathlength and from absorption coefficients. Therefore, this is an absolute, highly specific, and nearly interference-free measurement method that can be considered as a reference method (Biermann et al., 1988; Appel et al., 1989; Winer and Biermann, 1989).

DOAS has been used to measure several chemical species in the atmosphere, including NO, NO<sub>2</sub>, HONO, NO<sub>3</sub>, HCHO, SO<sub>2</sub>, O<sub>3</sub>, and OH (Biermann et al., 1988; Appel et al., 1990; Winer and Biermann, 1989; Fried et al., 1997). Several species can be monitored simultaneously. The detection limits for NO are around 1 ppb (Plane and Nien, 1992; Plane and Smith, 1995; Finlayson-Pitts and Pitts, 1986). DOAS is commercially available from several vendors.

TTFMS is similar to FTIR in that it is used to determine the concentration of small molecules that have fairly simple absorption spectra in the infrared (e.g., NO, NO<sub>2</sub>, HNO<sub>3</sub>, PAN, H<sub>2</sub>O<sub>2</sub>, and others, see Hansen, 1989; Cooper et al., 1994). However, in TTFMS a diode laser is the light source, which is modulated simultaneously at two arbitrary but closely spaced frequencies. The beat tone between these two frequencies is monitored as the laser carrier and associated sidebands are tuned through an absorption line (Hansen, 1989). The TTFMS is highly specific and extremely sensitive, with detection limits for a number of species, including NO, in the ppt range. The measurement cell can either be a low-pressure, multiple-reflection optical cell with pathlengths of 100 m or more, which provides the best sensitivity, or measurements can be made in situ (i.e., at atmospheric pressure) with a long-pathlength, multiple-reflectance system similar to the FTIR. Only research grade instruments are available and no specific information was found regarding accuracy.

LIF relies on the absorption of radiation by NO in the sampled air, followed by the detection of fluorescence from the excited NO (Bradshaw et al., 1985; Sandholm et

al., 1990). A more detailed description of the method for NO,  $NO_2$ , and  $NO_x$  is given in Sandholm et al. (1990). LIF is sensitive and relatively free from interferences with limits of detection in the low ppt range. Comparisons of chemiluminescence and LIF methods for NO at ground level and aloft from aircraft platforms have shown agreement to within 30% in the concentration range of 5 to 200 ppt (Hoell et al., 1984; Gregory et al., 1990a).

## Nitrogen Dioxide (NO<sub>2</sub>)

Several methods are available for the measurement of nitrogen dioxide in the atmosphere. These include the O<sub>3</sub>/NO chemiluminescence method after reduction of NO<sub>2</sub> to NO, the luminol fluorescence method, and four spectroscopic techniques: tunable diode laser absorption spectroscopy (TDLAS), differential optical absorption spectroscopy (DOAS), two-tone frequency modulated spectroscopy (TTFMS), and laser induced flourescence (LIF).

The most widely used method for the measurement of NO<sub>2</sub> involves the reduction of NO<sub>2</sub> to NO followed by detection of NO using the O<sub>3</sub>/NO chemiluminescence detector (Fontijn, 1970; Ridley and Howlett, 1974) described above. Reduction can be performed at a surface, catalytically or thermally, or photolytically in the gas-phase. Reduction of NO<sub>2</sub> to NO at a surface includes the use of a heated catalyst (molybdenum or gold in the presence of CO) (Dickerson et al., 1984; Fehsenfeld et al., 1987; Fahey et al., 1985) or chemically using FeSO<sub>4</sub> (Winfield and Buffalini, 1977; Stedman et al., 1977; Dickerson, 1984; Ridley et al., 1988a, 1988b). NO<sub>2</sub> concentrations are then determined by difference. The reduction of NO<sub>2</sub> to NO by these methods is not specific and a number of other nitrogen-containing species can interfere with the measurement of NO2 (e.g., HNO<sub>3</sub>, PAN, NH<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, HONO, and NO<sub>3</sub>) resulting in an overestimation of NO<sub>2</sub> by these methods (Winer et al., 1974; Cox, 1974; Grosjean and Harrison, 1985; Bollinger et al., 1983; Dickerson, 1985). Therefore, the thermal catalytic method is used to measure NO, and then NO plus other nitrogen oxides as a group (NO<sub>x</sub> or NO<sub>y</sub>). If the group is not well defined, it will be referred to in this report as NO<sub>x</sub>, since the species included in the group depend on a number of factors, such as inlet and line losses. With the proper design, all gas-phase nitrogen oxide species can be measured and this group is referred to

as NO<sub>y</sub> (Bollinger et al., 1983; Logan, 1983; Dickerson, 1985; Fahey et al., 1985; Fehsenfeld et al., 1987; Kelly et al., 1989). The measurement of NO<sub>y</sub> is discussed in more detail below.

In the photolytic reduction method, NO<sub>2</sub> is first photolytically reduced to NO using UV radiation, and then measured using the ozone/NO chemiluminescence detector (Kley and McFarland, 1980). Reduction by this method is specific to NO<sub>2</sub> and other oxides of nitrogen do not interfere with the measurement; however, the method is not as simple as surface reduction methods. NO<sub>2</sub> concentrations are then determined by difference. A description of the method and the performance of the photolytic instruments are discussed in detail by Parrish et al. (1990) and Fehsenfeld et al. (1990).

The luminol method (Maeda et al., 1980; Wendel et al., 1983; Schiff et al., 1986; Drummond et al., 1989a, 1989b) measures NO<sub>2</sub> directly by detecting the chemiluminescence produced when NO<sub>2</sub> reacts with a specially formulated solution containing water, luminol, Na<sub>2</sub>SO<sub>3</sub>, NaOH, and alcohol ("Luminol II" solution) in proportions chosen to enhance the sensitivity and minimize interferences. The signal is proportional to the chemiluminescence from the luminol oxidation. The instrument is very sensitive with a detection limit (2 sigma) of 5 ppt if zeroed every 30 min or 50 ppt if zeroed daily. Fehsenfeld et al. (1990) observed a 5 ppt detection limit using only a 3 sec integration of zero air and 1 ppt for a one minute integration, during an intercomparison study. The response time of the Luminox<sup>R</sup> instrument is fast (1 for a 10-ppb step change; Fehsenfeld et al., 1990) relative to the more sensitive chemiluminescence instruments, and along with its high sensitivity, small size, and low power consumption, makes the Luminox<sup>R</sup> instrument suitable for NO<sub>2</sub> measurements aloft from aircraft. However, the detector is sensitive to changes in pressure (i.e., changes in altitude) and temperature; but these can be corrected for mathematically if simultaneous pressure and temperature measurements are obtained (Bubacz et al. 1987; Kelly et al. 1990; Drummond, 1989b, 1991). Several groups have used the Luminox<sup>R</sup> instrument for sampling NO<sub>2</sub> aloft from aircraft (Kelly et al., 1990; Solomon and Thuillier, 1994).

Known interferences for the measurement of NO<sub>2</sub> by the luminol method are O<sub>3</sub> (1% or less of the O<sub>3</sub> concentration, measured as NO<sub>2</sub>) and PAN (0-70% of the PAN concentration measured, as NO<sub>2</sub>) (Sacco, 1989; Wright et al., 1989; Kelly et al., 1990;

Fehsenfeld et al., 1990). These interferences can become significant at NO<sub>2</sub> levels below 1-2 ppb (Drummond et al., 1989a; Fehsenfeld et al., 1990). Species shown to produce no measurable interferences at their normal atmospheric concentration ranges include NO, HNO<sub>3</sub>, HONO, NO<sub>3</sub>, SO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, HCHO, CO, and CO<sub>2</sub> (Schiff et al., 1986).

The signal below 2 ppb is nonlinear, but methods for treating the signal in the nonlinear range have been described (Drummond et al., 1989b; Kelly et al., 1990). An ozone scrubber also has been developed to minimize the ozone interference (Drummond et al., 1989a; 1989b); however, it also appears to remove up to 50% of the NO<sub>2</sub> at low concentrations. PAN interferences are a constant fraction of the PAN mixing ratio, although the fraction may depend on the batch and the age of the luminol solution (Sacco, 1989; Fehsenfeld et al., 1990). For a given batch of luminol, the PAN interference can be subtracted from the measured NO<sub>2</sub> concentration if simultaneous PAN measurements are obtained. An NO<sub>2</sub> reduction chamber also can be added upstream of the detector in a second sample line split off the inlet sample line (Drummond et al., 1989b; Jassim et al., 1993; Drummond et al., 1991). This allows for an ambient zero to be obtained, since the NO<sub>2</sub> is removed and only interferences pass through to the detector. NO<sub>2</sub> is then determined by difference.

A commercial luminol-based instrument is available that also measures PAN (Unisearch Associates, Inc., Ontario, Canada), which will be discussed later.

TDLAS, DOAS, and TTFMS methods were discussed earlier regarding the measurement of nitric oxide. Limits of detection for NO<sub>2</sub> for these methods range from about 1 ppb for DOAS to the low ppt range for TDLAS and TTFMS. During a NASA project, the TDLAS was operated aboard an aircraft by Unisearch Associates (Gregory et al., 1990b; Schiff et al., 1990). Only minor modifications were needed to the current ground-based system to make measurements aloft; however, the TDLAS showed a high bias both on the ground and in the air relative to high sensitivity chemiluminescence instruments at low concentrations. A two-photon laser-induced fluorescence system is also described by Sandholm et al. (1990) and reviewed by Parrish and Fehsenfeld (1998), however, this is strictly a research instrument. A comparison of airborne NO<sub>2</sub> measurements methods (O<sub>3</sub>/NO and photolytic chemiluminescence, TDLAS, and LIF) aboard aircraft platforms was conducted by Gregory et al. (1990b). Results indicated that

at low ambient mixing ratios, below 200 ppt, the methods agreed to within 30-40 % aboard the moving aircraft platforms.

## Total Reactive Nitrogen Oxides (NO<sub>y</sub>)

As mentioned earlier, NO<sub>v</sub> refers to the true sum of all gas-phase reactive oddnitrogen oxide species:  $NO + NO_2 + HNO_2 + NO_3 + PAN + NO_3 + HONO + 2N_2O_5 + PAN + NO_3 +$ aerosol nitrate + organic nitrates + etc. (Bollinger et al., 1983; Logan, 1983; Dickerson, 1985; Fahey et al., 1985; Fehsenfeld et al., 1987; Kelly et al., 1989). Measurement of NO<sub>v</sub> is performed taking advantage of the interference of reactive nitrogen species during thermal reduction of NO<sub>2</sub> to NO on a gold coated surface in the presence of CO or H<sub>2</sub> or on a heated molybdenum oxide surface. The NO produced is subsequently detected using an O<sub>3</sub>/NO chemiluminescence detector as describe earlier. To avoid losses in the sampling line and inlet, the reduction chamber is moved to the front of the inlet line, which results in only NO passing through the inlet line to the detector. Thermal Environmental Inc. manufactures the only commercially available NO<sub>y</sub> monitor. They modify their standard and high sensitivity units, moving the reduction chamber to the inlet. These units or individually modified units have been used in recent ozone and aerosol field programs (Wright and Roberts, 1996; Blumenthal et al., 1997b). Comparison of NO<sub>v</sub> monitors using different reduction surfaces have been performed at the surface and aloft (Fehsenfeld et al., 1987). Parrish and Fehsenfeld (1998) review these comparisons and indicate that while these monitors are suitable for measurements at ground level, problems have been noted for measurements aloft from aircraft platforms.

#### Nitrate Radical (NO<sub>3</sub>)

Measurement of nitrate radical is important for understanding nighttime production of HNO<sub>3</sub>, which can be an important pathway for removal of NO<sub>2</sub> from the atmosphere (Smith et al., 1995). It also may be important in the formation of HNO<sub>3</sub> under wintertime cloudy conditions in the western US where high levels of aerosol nitrate are observed during extended cool foggy periods, e.g., San Joaquin Valley of California.

The nitrate radical is measured at the ppt concentration level and nearly free from interferences by DOAS (Plane and Nien, 1992; Winer and Biermann, 1989 and references cited therein; Biermann et al., 1988; Finlayson-Pitts and Pitts, 1986 and references cited therein; Plane and Smith, 1995). Detection limits for nitrate radical by DOAS are in the few ppt range (Smith et al., 1995). The method is briefly described earlier under the nitric oxide section. Instruments are available commercially from several sources.

# Nitrous Acid (HNO<sub>2</sub>)

Continuous and integrated methods have been developed for the measurement of HNO<sub>2</sub> or as it is often written, HONO. Continuous methods rely on the spectroscopic determination of HONO, while integrated methods rely on the collection of HONO on a reactive surface followed by subsequent analysis of nitrite by either colorimetric methods or ion chromatography. Spectroscopic methods include TDLAS, DOAS, and FTIR. The latter has a poor detection limit for HONO, on the order of 10 ppb (Tuazon et al., 1980), which makes the method not suitable for most ambient applications. DOAS, described above, has reported limits of detection below about 0.5 ppb (Platt and Perner, 1980; Appel et al., 1990; Winer and Biermann, 1989). Appel et al. (1990) compared a DOAS to the annular denuder method. The methods were highly correlated (r=0.94) and on the average agreed to within 10%, with DOAS showing a systematic high bias of 10%. Uncertainty in the DOAS measurement for HONO was estimated at about 30%. An additional spectroscopic method is described in Parrish and Fehsenfeld (1998), UVphotofragment/LIF, but it has been applied in only a limited sense and will not be described here. Time-integrated methods, for the determination of HONO, employing a collection surface or substrate followed by chemical analysis in the laboratory will be discussed later in Section A.2.

## Peroxyacetyl Nitrate (PAN) and Other Organic Nitrates

Two GC methods and two spectroscopic methods are available to measure PAN in the troposphere. The two GC methods differ in their detector, one being an electron capture detector (GC-ECD) and the other being the luminol chemiluminescence detector (GL-L). PAN has most often been measured in the troposphere using GC-ECD (Singh and Salas, 1983; Drummond et al., 1989a, 1989b; Blanchard et al., 1990; Ridley et al., 1990; Williams and Grosjean, 1990 and references cited therein). However, GC-ECD instruments specifically designed to measure PAN in ambient air are not available commercially. In the GC-ECD method, PAN is separated from other reactive nitrogen oxides, including other organic nitrates by gas chromatographic and then determined based on its retention time by the ECD. Calibration of the detector requires the injection of PAN into the system. Quantification is usually based on peak area.

The GC luminol method was first described by Burkhardt et al. (1988). In this method, PAN is separated from NO<sub>2</sub> and other organic nitrates by gas chromatography, as with the GC-ECD. However, PAN eluting from the GC column is thermally reduced to NO<sub>2</sub> prior to detection, and then measured using the same luminol detector as described above for the luminol chemiluminescence measurement of NO<sub>2</sub>. The more reactive oxides of nitrogen, such as HNO<sub>3</sub>, HONO, NO<sub>3</sub>, and other reactive interfering species, such as ozone, are retained on the column (Burkhardt et al. 1988). NO, while passing through the GC column, is not detected by the luminol detector. This method is available commercially.

The GC-L method has been compared to the GC-ECD methods (Drummond et al., 1990; Blanchard et al., 1990, also see Solomon and Thuillier, 1994). In general, the results indicated that the two methods agree to within 20-30 percent and that the GC-L method can provide accurate, continuous, and sensitive measurements of ambient PAN concentrations down to about 25 ppt (Blanchard et al., 1990).

One major advantage of the GC-L PAN monitor compared to the GC-ECD is the method of calibration. The GC-ECD requires calibration by PAN in the field, which is difficult to do accurately because of the poor stability of PAN at ambient temperatures;

although methods have been described (see for example Gregory et al. 1990c). On the other hand, the GC-L instrument is calibrated in the laboratory with PAN under controlled conditions to obtain the column efficiency, and then the detector can be calibrated in the field with NO<sub>2</sub>, which is much more stable than PAN. This advantage is realized since PAN is quantitatively converted to NO<sub>2</sub> before detection, and the luminol detector is specific for NO<sub>2</sub>.

The first use of the luminol PAN instruments in a regional study in the US was during the 1990 San Joaquin Valley Air Quality Study. PAN monitors (Unisearch Model LPA-4) were operated for nearly 2 months at 10 sites and collocated with a suite of other gas-phase and aerosol phase measurements (see Solomon, 1994b for a description of the study). The PAN monitors were calibrated in the laboratory with PAN prior to shipping and several times in the field, as well. For one week during the study, the luminol monitor was compared to a GC-ECD. Results indicated a significant bias between the two monitors. A detailed laboratory experiment comparing the two monitors was conducted immediately after the study, using simultaneous sampling from a chamber. Results were more consistent after correcting a problem with the calibration of the GC-ECD. An overall uncertainty was assigned to the PAN luminol measurements of about 25% (see Solomon and Thuillier, 1994).

In situ atmospheric concentrations of PAN are determined by measuring the absorption of PAN in the infrared wavelength region. When applied to ambient measurements, FTIR is combined with a long-pathlength, multiple-reflectance system to yield optical pathlengths of 1-2 km (Biermann et al., 1988 and references cited therein; Finlayson-Pitts and Pitts, 1986 [see pp. 319-337 for a brief summary of the technique and additional references]). Moderately low limits of detection (<a few ppb), applicable to ambient measurements in polluted air are obtained by the use of long-pathlengths. This is a direct measurement of PAN and ambient concentrations are determined from absorption coefficients. Therefore, this is an absolute, highly specific, nearly interference-free measurement method that can be considered as a reference method (Biermann et al., 1988; Hering et al., 1988).

Besides PAN, a number of other species can be measured by long-path FTIR, including HNO<sub>3</sub>, NH<sub>3</sub>, HCHO, and HCOOH. Detection limits for these species are about

1-4 ppb (Biermann et al., 1988; Finlayson-Pitts and Pitts, 1986 [see pp. 319-337]). This poor sensitivity, relative to many of the other methods, is considered to be the major disadvantage of the method. However, since the FTIR is considered a reference method, it is recommended for QA/QC purposes, especially since PAN, HNO<sub>3</sub>, and NH<sub>3</sub> concentrations can be measured simultaneously.

PAN can also be measured at ppt concentrations by TTFMS as described above.

PAN is the dominant organic nitrate species found in ambient air and is observed in urban areas at peak concentrations of a few ppb to tens of ppb (Grosjean, 1983; Tsalkani et al., 1991; Solomon and Thuillier, 1994). Measurement of other organic nitrate compounds have been obtained in several areas as well, typically with total concentrations of only a few hundred ppt (Flocke et al., 1991; O'Brian et al., 1995). These species are determined by collection on charcoal traps, Tenax, or cooled glass beads and quantified by GC-ECD, GC-L, or GC-chemiluminescence as described earlier (Atlas and Schauffler, 1991; Bertman et al., 1995; O'Brian et al., 1995; Hao et al., 1994; Flocke et al., 1991). O'Brian et al. (1995), for example, quantified 17 organic nitrates in atmospheric samples collected at a rural site in Ontario, Canada using charcoal traps and quantified using both GC-ECD and GC-L methods. The concentration of total organic nitrates ranged from 12-140 ppt, excluding PAN. Measurement of these species helps to understand peroxy radical chemistry, as the peroxy radicals are precursors to these species and play a significant role in the ozone formation processes (see discussions in Flocke et al., 1991 and in Finlayson-Pitts and Pitts, 1986).

#### Nitric Acid (HNO<sub>3</sub>)

Continuous and integrated methods have been developed for the measurement of HNO<sub>3</sub>. However, suitable (continuous, high sensitivity, easy to use) methods are not yet available; although a new approach is undergoing evaluation and field testing (Edgerton, 1998, private communication) and will be briefly described below. The most widely used methods involve the use of reactive filters and/or diffusion denuders (see for example Lawson, 1988 for results of an extensive intercomparison of many of these methods). These methods have been problematic due in part to the partition of nitrate

among the gas, particle, and liquid droplet phases, which is a function of temperature, relative humidity, aerosol composition, and the reactive nature of HNO<sub>3</sub> (Hildemann et al., 1984; Russell and Cass, 1986). Filter and denuder based methods for determining time-integrated concentrations of HNO<sub>3</sub> are discussed in Section A.2.

Several research methods, based on spectroscopic determination of HNO<sub>3</sub>, with varying levels of sensitivity, have been developed; however, they require highly trained operators. Spectroscopic methods include TDLAS, FTIR, and TTFMS. These methods have been described earlier in regards to the determination of NO and PAN. Detection limits for these methods for HNO<sub>3</sub> range from about 4 ppb for FTIR, to about 0.5 ppb for TDLAS, to less than 0.001 ppb for the TTFMS. Of these methods, only the TDLAS is available commercially, yet it still requires a well-trained operator. TDLAS was compared to a filter-based method and a denuder method for the collection of HNO<sub>3</sub> aboard aircraft (Gregory et al., 1990d). Results were mixed and at times differed by a factor of two at HNO<sub>3</sub> concentrations < 500 ppt.

A recently developed method, chemical ionization mass spectroscopy, provides for the continuous, fast-response, molecular-specific determination of HNO<sub>3</sub> with limits of detection in the 10 ppt concentration range (Huey et al., 1998; Mauldin et al., 1998). However, as with the spectroscopic methods, the CIMS is still in the research stage of development. CIMS is not a direct measurement of HNO<sub>3</sub>, but relies on the equilibrium between HNO<sub>3</sub> and a reactant ion, e.g., SiF<sub>5</sub> or HSO<sub>4</sub> (Huey et al., 1998; Mauldin et al., 1998). Comparison of CIMS with filter packs for the measurement of HNO<sub>3</sub> (Fehsenfeld et al., 1998) reaffirmed that the collection of HNO<sub>3</sub> by Teflon/nylon filter packs results in a positive bias for HNO<sub>3</sub> due to volatilization of particulate ammonium nitrate from the Teflon pre-filter (see e.g., Hering et al., 1988 and references cited therein).

A recently developed method (Edgerton, 1988, private communication) uses two high sensitivity NO<sub>y</sub> monitors and a nylon filter on one channel to remove HNO<sub>3</sub> from that channel. Nitric acid is then determined by difference. The method is currently being evaluated.

## Ammonia (NH<sub>3</sub>)

Continuous and integrated methods have been developed for the measurement of NH<sub>3</sub> in the troposphere. The most widely used methods, historically, involve the use of reactive filters and/or diffusion denuders (see for example Wiebe et al., 1990; Appel et al., 1988 for results of an extensive intercomparison of many of these methods). Filter and denuder based methods for determining time-integrated concentrations of NH<sub>3</sub> are discussed in Section A.2.

Recently, an O<sub>3</sub>/NO chemiluminescence monitor has been modified to measure NH<sub>3</sub> continuously with a limit of detection around 1 ppb (Kita, Thermal Environmental Instruments, private communication). This continuous sampler has a proprietary converter that allows for the measurement of NO, NO<sub>x</sub> or NO<sub>y</sub>, and NH<sub>3</sub> separately by switching between three channels rather than two as is done in the standard NO/NO<sub>x</sub>/NO<sub>y</sub> monitor. This is a relatively new instrument, that is commercially available. The monitor needs to be calibrated in the field with NH<sub>3</sub>, and low levels of NH<sub>3</sub> are difficult to obtain. NH<sub>3</sub> losses in the inlet and tubing to the monitor can severely limit levels of detection in ambient air (Parrish and Fehsenfeld, 1998). However, this is the only continuous commercially available method that has low limits of detection and does not require highly trained operators. Calibration and long inlet lines can be problematic however.

Several continuous wet chemical flow techniques are summarized in Parrish and Fehsenfeld (1998). Of the methods reviewed by these authors, the one that showed the most promise for continuous NH<sub>3</sub> measurements was described by Genfa et al. (1989). In this method, NH<sub>3</sub> diffuses through a porous membrane into water where the dissolved NH<sub>3</sub> reacts with a reagent that results in fluorescence from the reaction product. The method is calibrated against known standards, is relatively inexpensive, is specific for NH<sub>3</sub>, and has a limit of detection below 50 ppt for a 5-min average sample time.

Several spectroscopic methods for the determination of NH<sub>3</sub>, with varying levels of sensitivity, have been developed; however, most require highly trained operators. Spectroscopic methods include TDLAS, DOAS, FTIR, and TTFMS. These methods have been described earlier with regards to the determination of NO and PAN. Detection

limits for  $NH_3$  by these methods range from about a few ppb or less for FTIR and DOAS, to about <0.5 ppb for TDLAS, to less than 0.001 ppb for the TTFMS. Of these methods, only DOAS is available commercially.

As mentioned for the measurement of HNO<sub>3</sub>, chemical ionization mass spectroscopy, appears to be promising for the determination of NH<sub>3</sub> with limits of detection in the low ppt concentration range (Ziereis and Arnold, 1986; also see Parrish and Fehsenfeld, 1998). However, as with the spectroscopic methods, the CIMS is still in the research stage of development and requires highly trained personnel to operate. Parrish and Fehsenfeld (1998) also mention several other research grade methods for measuring NH<sub>3</sub>, including CO<sub>2</sub> differential absorption lidar (DIAL) and an LIF method. The reader is referred to Parrish and Fehsenfeld (1998) for additional information on these methods.

The National Oceanic and Atmospheric Administration (NOAA) will be conducting an NH<sub>3</sub> methods comparison during the winter of 1998-1999. The study will involve comparison of a high time resolution citric acid denuder-filter pack system, a modification of the ozone/NO chemiluminescence system described above, and a CIMS. Results from this evaluation should provide additional information on the precision, accuracy, and reliability of these methods to measure ambient ammonia concentrations in a nearly continuous manner (Fehsenfeld, NOAA, private communication, 1998).

#### **A.1.2 Carbon-Containing Species**

Compounds in the gas-phase containing carbon represent an extremely complex mixture in the atmosphere. The most abundant species are CO, CO<sub>2</sub>, and CH<sub>4</sub>, however, hundreds of species containing carbon, hydrogen, and heteroatoms, such as oxygen and nitrogen are also present in the gas-phase. This section describes methods for the measurement of CO, CO<sub>2</sub>, and CH<sub>4</sub>, of hydrocarbons containing only carbon and hydrocarbons, and of oxygenated hydrocarbon species. Major subgroups include non-methane hydrocarbons (hydrogen and carbon compounds only) and volatile organic compounds (VOC) containing hydrogen, carbon, and possibly oxygen.

#### Carbon Monoxide (CO)

The EPA reference method for measuring CO continuously in air uses nondispersive infrared spectroscopy (NDIS) (Informatics, 1979). A time-integrated method is below. In NDIR spectroscopy, infrared light from a conventional light source passes through two parallel cells, one which is the reference cell and contains a non-adsorbing gas and the other the sample cell with ambient air passing continuously through it. The difference in the signals is proportional to the CO concentration in air and quantitative results can be obtained when calibrated against known standards. The limit of detection for CO is about 1 ppm, which is well below concentrations observed in ambient air. Lower limits of detection (<100 ppb) also have been obtained with a modified gas filter correlation NDIS (Dickerson and Delany, 1988). TDLAS is capable of measuring CO at levels below 250 ppt. An intercomparison of the gas filter correlation (GFC) NDIS and TDLAS showed agreement to better than 10 % (Fried et al., 1991). The precision of the GFC NDIS was about 10% and that of the TDLAS was about 4%. Several other continuous spectroscopic and chemical methods are described in Parrish and Fehsenfeld (1998) and in Finlayson-Pitts and Pitts (1986) and the reader is referred to these sources for more information. Parrish and Fehsenfeld (1998) also describe a recently developed method based on vacuum UV excited resonance fluorescence of CO that is sensitive (less than 1 ppb), precise (about 1-2 ppb), and accurate with a high time resolution, which makes it suitable for use aboard aircraft. An intercomparison between the UV instrument and TDLAS showed agreement to within 10 % on aircraft flights.

A time-integrated method for CO involves collection of an air sample in a pretreated canister followed by gas chromatographic separation followed by reduction of CO to CH<sub>4</sub> with detection by a flame ionization detection (GC-FID). The GC-FID method is described in more detail below, as determination of CO is obtained in conjunction with determination of non-methane hydrocarbon measurements.

# Non-Methane Hydrocarbons (NMHC), CO, CO<sub>2</sub>, and CH<sub>4</sub>

Measurements of NMHC (usually in the C<sub>2</sub>-C<sub>10</sub> carbon number range, although recent work has expanded the range to  $C_{20+}$ ) typically requires collection of a sample in the field, followed by chemical analysis of the sample in a laboratory at a later time. NMHC species contain, by definition, only hydrogen and carbon atoms. VOC species, which will be discussed later, include NMHC plus oxygenated hydrocarbons and perhaps other heteroatoms, which have been recently identified as comprising a significant fraction of the unidentified VOC, especially in rural areas (Rassmussen, personal communication). NMHC samples are collected in the field in canisters (C<sub>2</sub>-C<sub>10</sub>) or in cartridges containing an adsorbent (C<sub>8</sub>-C<sub>20+</sub>). Two analytical methods are generally used to determine concentrations of NMHC: GC-FID and GC-mass spectroscopy (GC-MS). GC-FID measures only NMHC under normal operating conditions and typical urban and rural atmospheric concentrations of hydrocarbons. FID is non-specific for hydrocarbons, thus the need to separate species using gas-chromatography, and has a sensitivity that is approximately linearly proportional to the number of carbon atoms in the hydrocarbon molecule (Ackman, 1968). GC-MS, on the other hand is capable of measuring NMHC and oxygenated hydrocarbons. In addition to NMHC, GC-FID also provides concentrations of CO, CO<sub>2</sub>, and CH<sub>4</sub>. A listing of typical NMHC species found in urban environments is given in Table A-2. Several low molecular weight oxygenated compounds are also listed. However, this list represents only the species typically determined for input to photochemical emissions-based models. Hundreds of compounds have been identified in tunnel studies and in the ambient environment when consideration is given to identifying peaks in the chromatogram that are typically referred to as "unidentified" (Gertler et al., 1996).

Speciated hydrocarbons also can be measured semi-continuously (one or two samples per hour) in the field using automated GC-FID, as is used in the Photochemical Assessment Monitoring Stations (PAMS) (Oliver et al., 1996). The number of species obtained using the automated method is more limited then those using time-integrated sampling followed by chemical analysis in the laboratory. Greenberg et al. (1994), Greenberg et al. (1996), Bottenheim et al. (1997), and Goldan et al. (1995) describe an

Table A-2. VOC Species and Corresponding Abbreviations.

Species	Abbreviation	Carbon Number	<b>Functional Group</b>	
ethane	ethane	2	alkane	
ethene	ethene	2	alkene	
ethyne	ethyne	2	alkene	
propane	propane	3	alkane	
propene	propene	3	alkene	
isobutane	ibutane	4	alkane	
isobutene	Ibutene	4	alkene	
1-butene	x1buten	4	alkene	
1,3-butadiene	x13butad	4	alkene	
butane	Butane	4	alkane	
trans-2-butene	t2buten	4	alkene	
2,2-dimethylpropane	x22dpro	4	alkane	
cis-2-butene	c2buten	4	alkene	
3-methyl-1-butene	x3mbute1	5	alkene	
isopentane	Ipentane	5	alkane	
1-pentene	Pentene1	5	alkene	
2-methyl-1-butene	x2m1bute	5	alkene	
pentane	Pentane	5	alkane	
isoprene	Isoprene	5	alkene	
trans-2-pentene	t2penten	5	alkene	
cis-2-pentene	c2penten	5	alkene	
2-methyl-2-butene	x2m2bute	5	alkene	
2,2-dimethylbutane	x22mbuta	6	alkane	
cyclopentane	Cypentan	5	alkane	
2,3-dimethylbutane	x23mbuta	6	alkane	
cis-4-methyl-2-pentene	c4mpnte2	6	alkene	
2-methylpentane	x2mpenta	6	alkane	
3-methylpentane	x3mpenta	6	alkane	
2-methyl-1-pentene	x2mpnte1	6	alkene	
1-hexene	x1hexene	6	alkene	
hexane	Hexane	6	alkane	
trans-2-hexane	t2hexene	6	alkene	
2-methyl-2-pentene	x2m2pnte	6	alkene	
cis-2-hexene	c2hexene	6	alkene	
methylcyclopentane	Mcypenta	6	alkane	
2,4-dimethylpentane	x24mpnta	7	alkane	
benzene	Benzene	6	aromatic	
cyclohexane	Cyhexane	6	alkane	
2-methylhexane	x2mhexan	7	alkane	

Table A-2. VOC Species and Corresponding Abbreviations (continued)

Species	Abbreviation	Carbon Number	<b>Functional Group</b>	
2,3-dimethylpentane	x23mpnta	7	alkane	
3-methylhexane	x3mhexan	7	alkane	
heptane	Heptane	7	alkane	
methylcyclohexane	Mcyhexan	7	alkane	
4-methyl-1-pentene	x4mpnte1	6	alkene	
2,4,4-trimethyl-2-pentene	x244t2pe	8	alkene	
2,5-dimethylhexane	x25mhexa	8	alkane	
2,4-dimethylhexane	x24mhexa	8	alkane	
2,3,4-trimethylpentane	x234mpta	8	alkane	
toluene	Toluene	7	aromatic	
2,3-dimethylhexane	x23mhexa	8	alkane	
2-methylheptane	x2mhepta	8	alkane	
3-ethylhexane	x3ethexa	8	alkane	
2,2-dimethylheptane	x22mhept	9	alkane	
2,2,4-trimethylhexane	x224mhxa	9	alkane	
octane	Octane	8	alkane	
ethylcyclohexane	Etcyhexa	8	alkane	
ethylbenzene	Etbenzen	8	aromatic	
m&p-xylene	Mpxylene	8	aromatic	
styrene	Styrene	9	aromatic	
o-xylene	Oxylene	8	aromatic	
nonane	Nonane	9	alkane	
isopropylbenzene	Iprobenz	8	aromatic	
n-propylbenzene	Nprobenz	8	aromatic	
p-ethyltoluene	Petoluen	9	aromatic	
o-ethyltoluene	Oetoluen	9	aromatic	
m-ethyltoluen	Metoluen	9	aromatic	
1,3,5-trimethylbenzene	x135tmbz	9	aromatic	
1,2,4-trimethylbenzene	x124tmbz	9	aromatic	
decane	Decane	10	alkane	
a-pinene	Apinene	10	alkene	
b-pinene	Bpinene	10	alkene	
methylstyrene	Mstyrene	10	aromatic	
1,2,3-trimethylbenzenze	x123tmbz	9	aromatic	
1,3-dimethylbenzene	x13dbenz	8	aromatic	
1,4-dimethylbenzene	x14dbenz	8	aromatic	
2,4,4-trimethyl-1-pentene	x244t1pe	8	alkene	
formaldehyde	formalde	1	carbonlyl	
acetaldehyde	acetalde	2	carbonyl	

Table A-2. VOC Species and Corresponding Abbreviations (continued)

Species	Abbreviation	Carbon Number	Functional Group	
Acetone	acetone	2	carbonyl	
propanal	propanal	3	carbonyl	
methylethylketone & butanal	mekbut	4	carbonyl	
pentanal & pentanone	penpan	5	carbonyl	
cyclohexanone	cyhex	6	carbonyl	
hexanal & hexanone	hexhex	6	carbonyl	
benzaldehyde	benzalde	7	carbonyl	

automated system with comparisons to the canister method. Several other methods for the determination of organic species in ambient air are in development. These have been summarized by Parrish and Fehsenfeld (1998).

## Hydrocarbon Sample Collection

Intermittent, time-averaged ambient air samples for hydrocarbon species analysis are usually collected in SUMMA® polished stainless steel canisters of various sizes (e.g., 6 1 for surface and 0.85 1 for aircraft measurements) (see description of method in Solomon and Thuillier, 1994 as specified by Rasmussen). These canisters are also analyzed for CO, CO<sub>2</sub>, and CH<sub>4</sub>. Stability of the hydrocarbons in these canisters during storage is good for most compounds; although losses of higher molecular weight species have been noted as well as a positive artifact for olefins (Holdren, 1979; Rasmussen, 1997 personal communication; Solomon and Thuillier, 1994 for results during SJVAQS). Finally, results of storage depend on the history of use and handling of the canister. Canisters need to be thoroughly cleaned before use and this process has been described by Rasmussen (1989) as adopted from EPA Method TO-14 (Winberry et al., 1988). A summary of the procedure is given in Solomon and Thuillier (1994) as applied in during the 1990 SJVAQS. Tedlar bags are also used for surface measurements following the same approach as for cannisters.

For collection of higher molecular weight hydrocarbons ( $C_{10}$ - $C_{20}$ ), samples are collected using cartridges filled with Tenax. Ambient air is drawn through these cartridges at constant flow rate, and then the samples are brought to the laboratory for chemical analysis (Biesenthal et al., 1997; also see description of method in Solomon and Thuillier, 1994 as specified by Rasmussen). Samples collected using TENAX can be analyzed by GC-MS, which also provides an estimate of higher molecular weight oxygenated compounds if large sample volumes are used. Measurement of low molecular weight carbonyl compounds, using a different adsorbent and analyzed by GC-liquid chromatography will be discussed later.

After sample collection in canisters, CO-CH<sub>4</sub>-CO<sub>2</sub> are determined by EPA method TO-12. In this method, these species are separated by gas chromatography using a packed column. Methane (CH<sub>4</sub>) is measured directly by a flame ionization detector (FID), while CO and CO<sub>2</sub> are first reduced to CH<sub>4</sub> over a Ni catalyst at 400°C and reported as CH<sub>4</sub>. An example of operating conditions is given in Solomon and Thuillier (1994).

## *Total Non-Methane Hydrocarbon (TNMHC)*

Total non-methane hydrocarbon in canisters is routinely determined using GC-FID according to the guidelines specified in EPA Method TO-12, as described above for CO-CO<sub>2</sub>-CH<sub>4</sub>. An example of operating conditions is given in Solomon and Thuillier (1994). This method detects hydrocarbons (compounds containing only hydrogen and carbon) with great sensitivity as well as hydrocarbons containing elements other than carbon and hydrogen (i.e., oxygen, chloride, and other heteroatoms). However, hydrocarbons containing heteroatoms are typically below the detection limit of the GC-FID, under usual operating conditions and sample size. However, because heteroatoms can be detected by this method, TNMHC is sometimes referred to as total non-methane organic carbon (TMNOC). Use of TNMHC implies that species containing other elements are corrected for or ignored.

## $C_2$ - $C_{10}$ Hydrocarbon Speciation Method

The method most often used for analysis of hydrocarbon species is EPA Method TO-14. This method is for analysis of hydrocarbons collected in SUMMA® canisters with analysis by GC-FID. An example of operating conditions is given in Solomon and Thuillier (1994) and Bottenheim et al. (1997). The GC-FID method typically uses a 500 ml sample. The method has been modified slightly by removing the dryer to prevent loss of monoterpenes. Samples are analyzed by directly trapping a 250 or 500 ml aliquot of

the sample on a stainless steel loop cold trap containing glass beads immersed in liquid oxygen. The trapped hydrocarbons are then desorbed into a capillary cryofocusing loop and separated using gas chromatography. Details of the procedure as applied by Rasmussen for samples collected during SJVAQS is given in Solomon and Thuillier (1994) and during Pacific '93 by Bottenheim et al. (1997). Detection limits observed during SJVAQS, by individual species, are given in Solomon and Thuillier (1994), and are in the range of 0.1-0.2 : g m<sup>-3</sup> or about 0.2 ppbC. Precision, based on analysis of duplicate samples collected during SJVAQS, is given for a series of compounds in Solomon and Thuillier (1994). Precision values for the most abundant species were in the range of 10-20 %. Poorer precision (in the range of 40-80 %), was reported for aromatic compounds and was likely do to the low ambient concentrations of these species in the duplicate samples. A discussion of a methods intercomparison study and of several methods still in development for determination of hydrocarbon species is described in Parrish and Fehsenfeld (1998).

## C<sub>7</sub>-C<sub>20</sub> Hydrocarbon (VOC) Speciation Analysis

For over 20 years, the analysis of VOC compounds in ambient urban air for  $C_2$  to  $C_{10}$  hydrocarbon speciation has been performed on air sample volumes of 100 to 500 ml. Standardization of GC-FID methods around these small volumes has been done (1) because this provides sufficient concentrations to accurately measure the  $C_2$  to  $C_{10}$  hydrocarbons in urban air in one processing step; (2) processing larger volumes of air is difficult, usually requiring several preparatory steps before the sample is cryofocused on the head of the column, and (3) due to the problem of frequent freeze-up [blockage] of the freezeout loop by the water vapor in sample volumes larger than 500 ml. Nafion® and other selective dryers have been used to remove the water, but all of them have some inherent problem. For example, Nafion® destroys most of the  $C_{10}H_{16}$  monoterpenes. Rasmussen (personal communication) has developed a single pre-concentration step to allow larger volumes (1,000 - 5,000 ml) of air to be used with a freezeout loop. Details of this method are given in Solomon and Thuillier (1994).

A comparison of the conventional method, using a 500 ml sample, to the improved method using the larger sample volume, both followed by GC-FID analyses was performed on 155 SJVAQS samples. The majority (>90%) of samples had TNMHC concentrations less than 200 ppbC. Correlation coefficients (r<sup>2</sup>) for most species compared were greater than 0.9 with an average r<sup>2</sup> value of 0.946 for total identified nonmethane hydrocarbons. The r<sup>2</sup> agreement between the methods for the total non-methane hydrocarbon values (identified plus unidentified) was 0.823. This is because the total unidentified hydrocarbon fraction compared with and a r<sup>2</sup> value of only 0.254. Obviously, the two methods do not agree on the amount of the unidentified hydrocarbons in their respective chromatograms; the method using a higher sample volume reports a smaller quantity of unidentified species in the C<sub>5</sub> to C<sub>10</sub> range. Since the method was developed with the objective of analyzing a 10-fold larger sample, to better measure the  $C_{10}$ + species, many of the small baseline peaks not normally seen or integrated by the conventional method in a 100-500 ml sample are now being better determined and identified. The only serious problem with the improved method is that two of the C<sub>2</sub> species (ethylene and acetylene) are poorly separated by the Carbotrap III sorbent bed when used with the 5000 ml samples. The r<sup>2</sup>, between the two methods, for these compounds is poor, 0.23 and 0.06, respectively. Surprisingly, ethane is well separated with a r<sup>2</sup> value of 0.90. However, what was lost in the chromatography of the C<sub>2</sub> fraction in the 5000 ml sample is gained in the higher molecular weight hydrocarbons, those species containing more carbons than decane  $(C_{10})$ .

"What percentage of the total VOC or hydrocarbon burden is in the  $C_{10}$  to  $C_{15}$  fraction?" is an important question. At present the California Air Resources Board (ARB) assumes that 3% of the TNMOC are greater than  $C_{10}$ . Form the analysis of the 155 SJVAQS/AUSPEX samples, using the improved method, a more robust value of 8  $\pm$  4% was measured. In this analysis, attention was focused on rural to cleaner suburban air samples with TNMOC values of 25 to 100  $\mu$ g/m<sup>3</sup>. No attempt was made to measure urban samples with concentrations of 200-500  $\mu$ g/m<sup>3</sup>, which possibly are more typical of the types of samples previously analyzed by ARB.

To verify GC-FID peak identifications and to determine what other NMHC compounds might be present in ambient air, samples also are analyzed by GC-MS full scan. This approach requires sample volumes from 500 ml (verification of GC-FID peaks) to sample volumes typically, in the range of 5000 to 50,000 ml. The larger sample size allows for determination of many of the smaller peaks that were in the conventional method, but too small for identification and quantification. GC-MS full scan sensitivities for most compounds are at 0.1 ppb or less (see Solomon and Thuillier, 1994 for SJVAQS). Bottenheim et al. (1997) report limits of detection in the range of 5-30 ppt with precision in the range of 20-40 ppt. Results from an intercomparison conducted by the National Center for Atmospheric Research, indicated agreement between participating laboratories of 3-15 %.

## Oxygenated Volatile Organic Compounds

Historically, more than 80-90 % of the hydrocarbon mass are identified by species in hydrocarbon samples collected in urban areas, whereas only 40 to 50% of the mass is identified in samples collected downwind of urban and rural areas (e.g., Magliano, 1996; Rasmussen, 1996; Lonneman and Seila, 1989). Recent results indicated that many of the unidentified peaks are oxygenated hydrocarbons (Rasmussen, 1996; Rasmussen, personal communication regarding results in SJVAQS, NARSTO-NE).

Over the last 10 years, low molecular weight (<C<sub>7</sub>) carbonyl species (aldehydes and keytones) have been the primary oxygenated species measured during regional field campaigns (see those listed at the end of Table A-2). More recently, a number of other species, as well as the low molecular weight carbonyls have been measured, including alcohols, esters, heterocyclic compounds, and carbonyl compounds (see Table A-3).

The standard method for measuring low molecular weight carbonyl compounds involves the collection of these species using C<sub>18</sub> Sep-Pak cartridges that have been impregnated with purified 2,4-dinitrophenylhydrazine (DNPH) and phosphoric acid (Fung and Grosjean, 1981; Tejada, 1986; Grosjean and Grosjean, 1995 and references

Table A-3. Oxygenated Hydrocarbon Analysis: GC-MS Sample Specifications

Alcohols	Aldehydes	Ketones	
Ethanol	Acetaldehyde	Acetone	
2-Propanol	Acrolein	Methyl-Vinyl Ketone	
2-Methyl-2propanol	Propanal	2-Butanone	
1-Propanol	2-Methylpropanal	3-Methyl-2-butanone	
2-Butanol	Methacrolein	2-Pentanone	
3-Methyl-1-pentanol	Butanal	4-Methyl-2-pentanone	
1-Hexanol	2-Butenal	2-Hexanone	
2-Ethyl-1-hexanol	Pentanal	4-Heptanone	
	Hexanal	2-Heptanone	
Esters	Heptanal	Cyclohexanone	
Methyl Formate	Benzaldehyde	3-Heptanone	
Ethyl Acetate	Octanal	6-Methyl-2-heptanone	
Butyl Formate	Nonanal	6-Methyl-5-heptan-3-	
		one	
Butyl Acetate	Decanal	2-Octanone	
Heptyl Formate	Cinnamaldehyde	Acetophenone	
	Undecanal	2-Nonanone	
<b>Heterocyclic Compounds</b>		2-Decanone	
Furan		2-Undecanone	
2-Methylfuran			
3-Methylfuran			
Tetrahydrofuran			

cited therein; Shepson et al., 1991; Grosjean and Grosjean, 1996). Detection limits less than 0.5 ppb have been obtained. Impingers have also been used; however, limits of detection are around 1-2 ppb (Kuwata et al., 1979; Grosjean and Fung, 1982). When ambient air is drawn through the cartridge containing DNPH, carbonyl species in the air sample react with DNPH to form hydrazones, which are separated and quantified using high-pressure liquid chromatography (HPLC) in the laboratory. Carbonyl species also have been quantified using GC-FID with detection limits ranging from <10 to 200 ppt (compound dependent) (Montzka et al., 1993).

Low molecular weight (<C<sub>10</sub>) volatile organic hydrocarbons can also be collected using canisters with analysis by GC-FID employing larger sample volumes or with GC-MS as described above for non-methane hydrocarbon species determination (Rasmussen, personal communication; and described in Solomon and Thuillier, 1994). The larger sample volumes, with either GC-FID or GC-MS, allow for identification and quantification of species that are normally below the limit of detection of the standard GC-FID method. Limits of detection are around 0.1 ppbC (see Solomon and Thuillier, 1994 results from SJVAQS/AUSPEX). Higher molecular weight VOC species are collected using TENAX cartridges and analyzed using GC-MS, as described above. Table A-3 provides a partial list of oxygenated species that might be measured using TENAX collection followed by GC-MS analysis or GC-FID with extended sample volumes. Chemical ionization mass spectroscopy also has been used to detect several oxygenated hydrocarbons at very low levels (see Parrish and Fehsenfeld, 1998 for summary of method).

Formaldehyde can be measured independently by several additional techniques, including two spectroscopic methods and two wet chemical methods. The wet chemical methods have been designed into continuous flow systems for in situ measurements. These include enzymatic fluorometry in which the fluorescence from an enzyme catalyzed reaction is detected (Heikes et al., 1996; Lazrus et al., 1988) and diffusion scrubbing (Fan and Dasgupta, 1994) or a glass coil scrubber (Kelly and Fortune., 1994) in which the fluorescence from the Hantzsch reaction with formaldehyde is detected. The spectroscopic methods include TDLAS (Fried et al., 1997) and DOAS (Harder et al., 1997a), which have been briefly described above. The DNPH/HPLC method for

formaldehyde was intercompared and validated against a long-path FTIR, a DOAS, and a tunable diode laser spectrometer in the 1986 Carbonaceous Species Methods Comparison Study (CSMCS) conducted by ARB in Glendora, CA (Fung and Wright, 1990; Lawson, et al., 1990). Results from this intercomparison indicated that DNPH/HPLC could provide reliable measurements of formaldehyde. Based on this evaluation, this technique was used to measure carbonyl compounds during SCAQS (Fung, 1989) and SJVAQS/AUSPEX (Fung et al., 1994). Kleindienst et al. (1988) compared four techniques for the measurement of formaldehyde in a rural environment (CH<sub>2</sub>O between 1-10 ppb). No systematic error was observed relative to sample spikes with and without a number of potentially interferring compounds (e.g., NO<sub>2</sub>, SO<sub>2</sub>, O<sub>3</sub>, and H<sub>2</sub>O<sub>2</sub>). Heikes et al. (1996) compared 5 methods for formaldehyde under pristine conditions (CH<sub>2</sub>O <350 ppt). Detection limits for the methods studied ranged form <10 ppt to about 100 ppt. The methods agreed reasonably well above 200 ppt, however, random variations in blanks lead to a poor correlation between methods below 200 ppt. Other comparison studies are described in Parrish and Fehsenfeld (1998).

## **A.1.3 Sulfur Containing Species**

### Sulfur Dioxide (SO<sub>2</sub>)

Several methods exist to measure SO<sub>2</sub> at ambient levels in the lower troposphere. Finlayson-Pitts and Pitts (1986) provide a listing of methods available in the mid-1980s, with relevant references. The methods listed include the paraosaniline method, which is the EPA reference method (EPA, 1982), fluorescence, GC-flame photometry, TDLAS, DOAS and several others. TDLAS and DOAS methods have been described briefly in Section A.1.1. Limits of detection for SO<sub>2</sub> range from 85 ppt for DOAS to 10 ppb for the reference method. Parrish and Fehsenfeld (1998) describe more recent developments in the measurement of SO<sub>2</sub> in the clean troposphere. Instruments described by Parrish and Fehsenfeld (1998) have limits of detection as low as a few ppt and readers are referred to references cited therein Parrish and Fehsenfeld for additional information.

Currently, the most widely used method is the pulsed fluorescence method, which is an EPA equivalent method (EPA, 1982). Fluorescence analyzers are based on the principle that SO<sub>2</sub> molecules absorb ultraviolet (UV) light and become excited at one wavelength, and then decay to a lower energy state emitting UV light at a different Certain hydrocarbon compounds interfere with the method but in wavelength. commercial instruments they are removed prior to the fluorescence chamber. H<sub>2</sub>O and NO also can interfere with the measurement. The interferences are less than 1 ppb for NO and less than 3% of SO<sub>2</sub> reading for H<sub>2</sub>O. The pulsating UV light source compensates for fluctuations in the UV light source. The fluorescence emitted by the excited SO<sub>2</sub> molecules is proportional to the SO<sub>2</sub> concentration and upon calibration is proportional to atmospheric SO<sub>2</sub> concentrations. Limits of detection are in the range of 0.06-0.2 ppb depending on the integration time. Precision is reported for commercial instruments at 1% of reading or 0.2 ppb. This is also the preferred method for use aboard aircraft platforms for the collection of SO<sub>2</sub>. It has three advantages over the FPM described below: it uses no consumable gases, has small zero drift with altitude, and its ouput is easily converted to mixing ratios (see discussion in Daum and Sprinston, 1993).

SO<sub>2</sub> also has been measured routinely by the flame photometric method (FPM); although it is used less often now. In this method, sulfur compounds are reduced in a hydrogen-rich flame to the S2 dimer. The emission resulting from the transition of the thermally excited dimer to its ground state at 394 nm is measured using a narrow bandpass filter and a photomultiplier tube. The response of the instrument is approximately proportional to the square of the sulfur concentration. Limits of detection with commercial instruments are in the 1 ppb range. The FPM has also been used to measure particulate-phase sulfur species, since the flame photometric detector responds to both particulate and gas-phase sulfur species. In this case, particulate sulfur compounds are measured continuously after gaseous sulfur compounds are selectively removed using a lead (II) oxide-glycerol coated denuder (Garber et al., 1983). Speciation between particulate sulfate, disulfate, and sulfuric acid by selective thermal decomposition is possible (Huntzicker et al., 1978; Cobourn et al., 1978). The FPM method has also been used aboard aircraft after appropriate modifications (see review by Daum and Springston, 1993).

## Other Sulfur-Containing Compounds

Several reduced sulfur-containing compounds have been measured in ambient air. These include hydrogen sulfide (H<sub>2</sub>S), carbonyl sulfide (COS), carbon disulfide (CS<sub>2</sub>), dimethyl sulfide (DMS), CH<sub>3</sub>SH, C<sub>2</sub>H<sub>5</sub>SH, (CH<sub>3</sub>)<sub>2</sub>S, and (CH<sub>3</sub>)<sub>2</sub>S<sub>2</sub>. Methods for the measurement of these species require collection/preconcentration and separation of the individual compounds followed by detection by a variety of methods. measurement methods for obtaining atmospheric concentrations of the reduced sulfur species are described in Parrish and Fehsenfeld (1998). Collection methods include cryogenic sampling or collection on a reactive substrate (e.g., gold wool or polymers), while separation of the species is done typically using gas chromatography. Detectors include flame photometry, mass spectroscopy, and electron capture detection. Several intercomparisons of methods available to measure these species have occurred for both ground-based and airborne platforms and these, along with a brief description of the methods, can be found in Parrish and Fehsenfeld (1998). The limits of detection of research grade methods are typically below 100 ppt and even below 10 ppt. A discussion of the measurement of important sulfur containing compounds associated with fog or cloud droplets is discussed in Section A.3.

### A.1.4 Atmospheric Oxidants

### Ozone

Methods available to measure ozone in the atmosphere include continuous monitors that measure ozone at a single point in space over time and long-path spectroscopic methods that provide time-averaged integrated ozone concentrations over path-lengths of 10-20 km. Point measurements include ultraviolet (UV) absorption, chemiluminescence, and chemical titration. Spectroscopic methods include DOAS and LIDAR (light detection and ranging). The UV photometric method is currently the most widely used method for measuring ambient concentrations of ozone and has been

designated as an equivalent EPA method for ozone in air (EPA, 1986). The UV method is based on the absorption of ultraviolet radiation at 254 nm by ozone molecules present in the monitor's absorption cell. The ozone signal is determined by the difference between ambient air containing ozone and ambient air with the ozone removed or scrubbed. The ozone concentration in the absorption cell is directly related to the magnitude of the attenuation and with proper calibration it is directly related to ambient concentrations of ozone.

The minimum detectable level of UV monitors is about 2-5 ppb. Accuracies and precision are on the order of 10-15 percent or 2-5 ppb, which ever is larger. Interferences with the UV measurement method include any gaseous component or fine particle that absorbs or scatters light at 254 nm. Gaseous inorganic compounds normally found in the atmosphere, including NO<sub>2</sub> and SO<sub>2</sub>, do not interfere, and particles are largely removed by a pre-filter. The most likely interferences with the measurement are gaseous hydrocarbon compounds that are strong absorbers at 254 nm and are either partially or completely absorbed onto the scrubber. Examples of potential interfering organic compounds are aromatic compounds, such as benzene and benzene derivatives (e.g., styrene, cresol, and nitro-aromatic species), and include species that are emitted from both anthropogenic and natural sources (Leston and Ollison, 1992; Kleindienst et. al., 1993). Interferences from hydrocarbons can account for a positive interference in the UV measurement for ozone of up to 40 ppb based on the concentration of the interferences occurring during peak ozone periods (Leston and Ollison, 1992). Kleindienst et al. (1993) observed about a 3% interference with O<sub>3</sub> measurements at typical ambient smoggy conditions.

Water vapor may also interfere with the UV method, but the interference only occurs when water vapor concentrations are high and variable. This interference appears to be due to the condensation of water vapor on imperfect absorption cell windows, thus changing the optical properties of the absorption cell (Meyer et. al., 1991). Use of absorption cell windows with fewer imperfections results in a smaller interference from water vapor.

The ozone/ethylene chemiluminescence method (ECL) is the Federal Reference Method for measuring ozone in ambient air (EPA, 1978). The ECL method is based on

the reaction of ozone with ethylene (CH<sub>2</sub>=CH<sub>2</sub> or C<sub>2</sub>H<sub>4</sub>), which produces formaldehyde in an electrically excited state that transitions to the ground state emitting light in the visible range. This reaction is rapid and specific for ozone and takes place in a chamber that is coupled to a blue-sensitive photomultiplier tube. Under controlled conditions, the signal produced by the ozone-ethylene reaction is proportional to the ozone concentration in the reaction chamber and with proper calibration it is proportional to ambient ozone concentrations.

The minimum detectable level of commercial ECL monitors is about 2-5 ppb. Accuracy and precision are on the order of 10-15 percent or 2-5 ppb, whichever is larger. The only major interference for measuring ozone by the ECL method is water vapor (Lodge, 1989; Leston and Ollison, 1992; Kleindienst et. al., 1993). Other components normally found in ambient air do not interfere with the measurement of ozone by the ECL method (Hodgeson et, al., 1970; Carroll et. al., 1972). The water vapor interference results in one-hour ozone concentrations that may be high relative to a "true value", i.e., a positive interference of 3-12 percent high humidities (EPA, 1986). Because this is a direct measurement of ozone, long-term changes in water vapor will affect the measured ozone concentration. However, this interference can be adjusted for by calibrating the ECL monitors at humidities expected during peak ozone periods as suggested by EPA (1986); however, this is rarely done.

Vertical profiles of ozone are obtained along a single vertical trajectory using balloon borne ozonesondes equipped with an electrochemical concentration cell (ECC) (Komhyr, 1969). These instruments are often launched together with meteorological rawinsondes that also simultaneously measure wind speed and direction, temperature, and relative humidity (See Section A.4). The ECC is composed of platinum electrodes in neutral buffered potassium iodide solutions of different concentrations in the anode and cathode chambers. When air containing ozone is brought into the cathode portion of the cell, an electrical current is generated that is proportional to the ozone flux through the cell. Ozonesondes were used recently in the NARSTO-Northeast ozone study (Lehrman et al., 1997). Limits of detection for the units used during that study were about 2-3 ppb with a precision of about 10% (Lehrman et al., 1997). Several oxidizing species can interfere with the measurement (Barnes et al., 1985; Lehrman et al., 1997). These

include NO and PAN, which result in a positive interference, and SO<sub>2</sub>, which results in a negative interference.

Ozone is measured remotely using DOAS, as described earlier for NO in Section A.1.1. Limits of detection are in the low ppb range with a precision of less than 30% (Plane and Nien, 1992). The limit of detection in DOAS depends on the concentration of the species present in air and its absorption coefficient, since quantification is determined by mathematically de-convoluting each species in the spectrum based on unique peaks for each species. The strongest singles are de-convoluted first as weaker singles are lost in the noise during the de-convoluting process. Ozone concentrations obtained by DOAS were compared to those obtained with UV absorption (Harder et al., 1997b) during periods of uniform ozone mixing. Results indicated agreement to within 7%, even though UV absorption is a point measurement and DOAS is a path-integrated measurement.

Vertical and horizontal cross sections or profiles of ozone are obtained remotely using differential absorption lidar (DIAL). These measurements can be obtained either at the surface, looking upward, or from aircraft using a downward facing DIAL. In this method, gas concentration profiles are determined by analyzing the lidar backscatter singles for two wavelengths, one tuned to the wavelength for the species of interest, in this case for ozone at about 300 nm and one slight off that wavelength. The difference in the magnitude between the backscatter signals at the two wavelengths is proportional to the ozone concentration. Like radar, the time for the single to return to the detector provides a measure of the distance the molecule is from the source, thus allowing for a cross section to be measured. DIAL provide nearly continuous measurements of ozone from about 50 m to 3 km with a minimal detection limit of about 10 ppb or so and depends on the wavelength employed. Ozone concentrations measured with DIAL, DOAS, and UV absorption were compared as part of the EUROTRAC Tropospheric Ozone Lidar Intercomparison Experiment (TESLAS). The methods agreed among each other within 30%.

## Peroxy Radicals (HO<sub>x</sub>, RO<sub>x</sub>)

Peroxy radicals (HO<sub>x</sub>) and organic peroxy radicals (RO<sub>x</sub>) can be measured by several techniques. The chemical amplifier (CA) will be discussed here, as it is the most widely used method, while the reader is referred to Parrish and Fehsenfeld (1998) for information on the LIF-FAGE and matrix isolation electron spin resonance (MIESR) methods. LIF-FAGE measures only HO<sub>2</sub>, while MIESR measures HO<sub>2</sub> plus RO<sub>2</sub>. The CA technique is describe by Hastie et al. (1991), Arias and Hastie (1996), and Cantrell et al. (1993). In this method, peroxy radicals (HO<sub>2</sub> and RO<sub>x</sub>) are mixed in a chemical reactor with elevated concentrations of CO and NO. The peroxy radicals enter into a chain reaction with NO and CO, oxidizing these species to CO<sub>2</sub> and NO<sub>2</sub> while recyling the HO<sub>2</sub> or RO<sub>2</sub>, thus producing a large number of NO<sub>2</sub> molecules per radical entering the system. The reactions and details of the system are given in Hastie et al. (1991) and Arias and Hastie (1996). Limits of detection are a few ppt and precision is given at about 35% or equal to the uncertainty of determining the chain length of the reaction. The NO<sub>2</sub> produced is then detected using luminol chemiluminescence as discussed earlier (See Section A.1.1). Parrish and Fehsenfeld (1998) describe results of an informal comparison of peroxy radical measurement methods between the CA and MIESR methods. The two techniques generally agreed to within 40%, except under polluted conditions, in which case the CA technique was lower than MIESR.

### Hydrogen Peroxide and Organic Peroxides

Several sensitive methods have been developed and inter-compared for the measurement of  $H_2O_2$  and organic peroxides (Staffelbach et al., 1996; Mackay et al., 1996). These include several wet chemical methods and one spectroscopic method. Wet chemical techniques include enzymatic with fluorometric detection (EDF) (Lazrus et al., 1986; Heikes, 1992), Fenton derivatization with fluorometric detection (Lee et al., 1993), and high performance liquid chromatography (HPLC) (Lee et al., 1995; Kok et al., 1995). Recent fog experiments in the California's Central Valley (see e.g., Solomon and Magliano, 1996) employed the EDF method and this will be discussed here. Readers are

referred to Parrish and Fehsenfeld (1998), Kok et al. (1995), and Lee et al. (1995) for a summary of the other two wet chemical methods.

The EDF method measures hydrogen peroxide and total organic hydroperoxides continuously using a dual channel instrument (Lazrus et al., 1986). In this method, peroxides and other soluble gases are collected in distilled water flowing through a coiled glass tube. The peroxides are then reacted with p-hydroxyphenylacetic acid and the enzyme peroxidase to produce a fluorescent biphenyl derivative. Spectroscopic monitoring of the fluorescence emission at 420 nm allows for the quantitative determination of peroxides in the aqueous solution. An estimate of the relative contribution of hydrogen peroxide to total hydroperoxides is measured by introduction of a second enzyme catalase into a second aqueous flow channel, to preferentially destroy hydrogen peroxide prior to quantification. The dual-channel instrument yields only semi-quantitative organic hydroperoxide information because catalase can also react with organic hydroperoxides. The principal interference is only problematic when the contribution of the organic hydroperoxides to total hydroperoxides exceeds 50%. In this situation, the accuracy of the hydrogen peroxide measurement is degraded significantly. However, the interference can be minimized by controlling the concentration of catalase to limit hydrogen peroxide destruction to 90% or less. However, the ability to quantify total hydroperoxides is unaffected. Calibration is accomplished with gas and liquid phase standards. The gas-phase standards permit quantification of any losses in the sample inlet lines. The method has a typical hydrogen peroxide detection limit of 20-30 ppt, with a 10% precision and 15% accuracy for gas-phase concentrations around 1 ppb. instrument has a time response of 30 seconds.

TDLAS is the only spectroscopic method for the measurement of hydrogen peroxide (Mackay et al., 1990; Mackay et al., 1996). The method was described earlier (Section A.1.1). Limits of detection are in the range of 50-100 ppt (30 min average) with a precision of 5% over a 24-hr period with an accuracy of about 20% (Mackay et al., 1996). An intercomparison of TDLAS, EDF, and HPLC methods is described in Mackay et al. (1996) and Staffelbach et al. (1996). Results were mixed with agreement at times being as close as 20% and at other times differences being as large as a factor of 2. A summary of these intercomparisons is given in Parrish and Fehsenfeld (1998).

## Hydroxyl Radical (OH)

The reader is referred to the summary of methods and intercomparisons among methods given in Parrish and Fehsenfeld (1998) and in Finlayson-Pitts and Pitts (1986). All methods described are non-routine and require skilled operators. However, the OH radical is likely the most important species to be measured to understand gas-phase oxidation processes in the atmosphere, thus it is essential to a comprehensive model evaluation (See Section 3.1). Historically, OH measurements have not been included in regional field programs due to the difficulty in the measurement, insufficient sensitivity, and problems with interferences. Current methods can now provide sufficient sensitivity (Parrish and Fehsenfeld, 1998). Methods described include fluorescence assay by gas expansion-LIF (FAGE-LIF), long-path absorption, and chemical ionization mass spectroscopy (CIMS).

## A.1.5 Hydrochloric Acid (HCl)

Hydrochloric acid can be monitored continuously by TDLAS (Pokrowsky and Herrmann 1981) with limits of detection below 1 ppb. More often, time-integrated measurements are obtained using denuders (Solomon et al., 1988a; Eldering et al., 1991). The TDLAS method was described earlier (see Section A.1.1) and the denuder methods are described in Section A.2.

### A.2 Measurements of Particulate Matter and Condensable Gases

This section presents methods commonly used to measure fine particle mass and its chemical components. Our intent is not to provide an exhaustive list of methods and their descriptions, since these methods are presented in different EPA reports and many have been recently reviewed by Chow (1995). Rather, we provide an overview of existing methods that can be used to select the most appropriate methods when designing a field program. Table A-4 provides a summary of the major methods available for the

Table A-4. Measurements of Particulate Matter (Mass and Chemical Composition by Filter-Based and Continuous In-Situ Methods).

Method	Parameter	Detection Limit	Precision	Accuracy	Interferences	References
Teflon Filter/Gravimetric (FRM)	Mass	2 μg/m <sup>3</sup>	5%	Since this is the FRM its accuracy is by definition 0%, however it is not possible to quantify it because there is no gold standard for particle mass	It does not collect all semivolatiles such as ammonium nitrate and organic carbon	Federal Register (1997)
Teflon Filter/IC	Sulfate	0.64 μg/m <sup>3</sup>	5%	5-10	none	Koutrakis et al. (1988); Solomon et al. (1988)
Teflon Filter/IC	Ammonium	0.1 μg/m <sup>3</sup>	5%	5-10	none	Koutrakis et al. (1988); Solomon et al. (1998)
Teflon Filter/pH	Hydrogen Ion	2.4 nmole/m³	5-10%	10-20%	Alkaline particles, some weak acids	Koutrakis et al. (1992)
Nylon Filter/IC	Nitrate	0.04 μg/m <sup>3</sup>	10%	20%	NO <sub>2</sub> may produce a positive bias; may be eliminated with HgO denuder	Koutrakis et al. (1988); Solomon et al. (1988)
Teflon Filter/IC	Nitrate	0.04 μg/m <sup>3</sup>	10%	20%	Some negative interference	Koutrakis et sl. (1998); Solomon et al. (1998); Hering et al. (1988)
Teflon Filter/XRF	Twenty Elements	0.5-2.5 ng/m <sup>3</sup>	see list of elements in note #2	10%-20%	Accuracy may vary with filter loading and particle composition	Watson et al. (1997)
Quartz Filter/Thermal Analysis	Elemental Carbon	0.12 μg/m <sup>3</sup>	5-10%	Not possible to quantify		Chow et al. (1993)
Quartz Filter/Thermal Analysis	Organic Carbon	0.12 μg/m <sup>3</sup>	10-20%	Not possible to quantify	Converting carbon to organic carbon may introduce a positive or negative bias	Chow et al. (1993)
Beta Gauge	Mass	5 μg/m³for 60 minute average	10%	Not possible to quantify because there is no gold standard for particle mass	Response depends on particle composition, also loses semivolatiles during sampling	Wedding and Weigand (1993)

Table A-4. Measurements of Particulate Matter (Mass and Chemical Compositon by Filer-Based and continuous In-Situ Methods) (continued)

Method	Parameter	Detection Limit	Precision	Accuracy	Interferences	References
Piezoelectric Microbalance	Mass	10 μg/m³ for 1 minute average	10%	Not possible to quantify because there is no gold standard for particle mass	Response depends on particle composition, and loses semivolatiles during sampling	Ward and Buttry (1990)
TEOM	Mass	5 μg/m³ for 10 minute average	10%	Not possible to quantify because there is no gold standard for particle mass	Response depends on particle composition, loses semivolatiles during sample heating	Patashnick and Ruprecht (1991)
CAMM	Mass	5 μg/m³ for 30 minute average	10%	Not possible to quantify because there is no gold standard for particle mass	Response depends on square root of particle density	Koutrakis et al. (1995)
Chemilumin-escent Sulfur Analyzer	Sulfate	0.05 µg/m³ for 12 minute average	5%	5%	Measures sulfur	Benner and Stedman 1990)
FPD Sulfur Analyzer	Sulfate	1 μg/m <sup>3</sup> for 60 minute average	5%	5%	Measures sulfur	Huntzicker et al. (1978)
Thermal/ Optical Carbon Analyzer	OC/EC	0.2 µg/m³ for 120 minute average	10%	Not possible to quantify	Measures carbon from which the organic carbon compound mass is estimated	Turpin and Huntzicker (1991)
Aethalometer	EC	for 1 minute average	5%	Not possible to quantify	Measures light absorption	Hansen and Rosen (1990)
ADI automated nitrate monitor	Nitrate	0.7 μg/m <sup>3</sup>	0.2 μg/m <sup>3</sup>	NA		Hering and Stolzenburg (1998)

Notes:

#1. For all filter based methods we have assumed a flow rate of 16.67 liters/minute and a sampling duration of 24 hours. The particle sampler can be the FRM, IMPROVE, Harvard Impactor or any other PM2.5 sampler. For fine particle collection sampler differences due to inlet geometries are negligible.

#2. The detection limits for the following elements were determined based on the assumptions of presented in note #1. Also we have assumed a 13.8 cm<sup>2</sup> filter deposit area for a 47mm Teflon filter. The aluminum (2.5ng/m<sup>3</sup>), silicon (1.4), sulfur (1.2), chlorine (1.8), potassium (1), calcium (1), titanium (0.5), vanadium (0.2), chromium (0.2), manganese(0.2), iron (0.1), nickel (0.1), copper (0.1), zinc (0.2), arsenic (0.3), selenium (0.2), bromine (0.2), cadmium (2), and lead (0.5).

measurements of particulate matter and its chemical components. Included in this table are estimates of the methods limit of detection, precision, accuracy, and potential interferences or artifacts.

#### A.2.1 Particle Mass

## Federal Reference Method

The U.S. Environmental Protection Agency has promulgated new National Ambient Air Quality Standards for fine particulate matter (particles with aerodynamic diameter, da ≤ 2.5 μm, PM-2.5). These new standards are in addition to those existing for PM10 (da ≤10m, fine plus coarse particles, 2.5 ≤ da≤ 10 μm). For both the PM-10 and PM-2.5 standards, the Federal Reference Method (FRM) is based on the gravimetric analysis of particles collected on filters over a period of 24 hours. Gravimetric analysis was selected because most of the particle mass data used for the epidemiological studies that found associations between mortality and morbidity outcomes and ambient particle exposures are based on this method (e.g. Dockery, et al., 1993; Ito and Thurston, 1996).

The Federal Register (1997) specifies sampler design, performance characteristics, and operational requirements of the PM2.5 FRM. Design specifications of FRM samplers include a modified SA-246 PM10 inlet that has been previously tested and approved for PM<sub>10</sub> compliance monitoring. Sampler air enters the inlet and is drawn through the WINS impactor that is designed to remove particles with an aerodynamic diameter greater than 2.5  $\mu$ m by impacting the particles on the bottom of an open-topped aluminum cylindrical container. The impacted particles are trapped at the bottom of the well on an oil-impregnated glass fiber filter. A Teflon filter is placed downstream of the WINS impactor to collect the fine particles.

FRM performance specifications require that constant volumetric flow rates  $(16.67 \pm 0.83 \text{ LPM})$  be monitored and recorded continuously with the temperature and pressure of the sample air entering the inlet and near the filter. FRM samplers are required to maintain the temperature of the filter during and after the sampling within  $\pm 5$  °C of concurrent ambient temperatures, regardless of heating and cooling from direct sun

or shade during and after sampling. The objective of this specification is to minimize losses of semi-volatile particles, such as ammonium nitrate and some organic compounds. Potential FRM designs use active ventilation of the enclosure that surrounds the filter holder and WINS impactor in order to attain the temperature performance specifications.

The designated FRM hardware has been tested by the EPA in several locations around the country, including Southern California, Birmingham, Alabama, and Phoenix, among others. The tests were conducted for the following reasons: a) to ensure proper mechanical functioning of the hardware; b) to assess the precision of the instrument based on collocated multiple samplers; and c) to compare the observations against other similar instruments that have been used in prior studies (e.g., the IMPROVE sampler). However, these tests did not evaluate the accuracy of a single filter-based method for the labile and volatile substances, such as ammonium nitrate and chloride, organic species, and water, which are continually in transition between the particle and gas phases. These substances can be lost or gained by the filter during or after sampling. Therefore, as known from extensive past experience, this technology is likely to be accurate for sulfate and other stable particulate components, but is subject to potentially large sampling errors for labile substances.

A priori it is expected that the performance of the FRM will be a function of the sampling location and time of year. For instance, relatively large errors are expected at locations like Southern California and Phoenix, where nitrate and semi-volatile organics are already known to constitute a substantial portion of fine particle mass (Solomon and Moyers, 1986; Solomon et al., 1989). At eastern U.S. locations, larger errors are expected during the winter than the summer because the contribution of nitrate is larger during the winter. Considering all of these factors, a credible evaluation of the FRM ought to demonstrate the relationship between method performance and particle composition over a comprehensive range of geographic locations, as well as for different seasons of the year. To date, there are few studies underway that aim to evaluate the accuracy of the FRM and, in general, filter-based gravimetric methods (see for example, a 6-8 city evaluation of the FRM collocated with denuder/filter based samplers, sponsored by EPRI in 1997-1998; Saxena, EPRI, Palo Alto, personal communication,

1998). Extensive field and laboratory studies are required to develop a systematic understanding of the physico-chemical parameters affecting the magnitude of the artifacts for semi-volatile inorganics and organics.

At this point, it is difficult to estimate the accuracy of the FRM and other filterbased methods mainly for two reasons: a) the lack of accurate semi-volatile organic measurements; and b) the limited data base of simultaneous measurements of fine particle mass and ammonium nitrate. Although an estimate of the accuracy of the FRM mass measurement cannot be provided at this time, it can be speculated that these filter-based methods will underestimate fine particle concentrations under certain conditions (see for example, Hering et al., 1988 and follow-on special issue papers; Ding et al., 1998; Hering and Cass, 1998). The extent of this bias will depend on the concentrations mostly of ammonium nitrate and semi-volatile organic species, temperature (greater losses at higher temperatures (Hering and Casss, 1998), relative humidity, variations in their relation to the corresponding volatile species during collection, and the handling of the filters following sample collection. However, the extent of bias is not a simple function, because given the same concentrations of ammonia and nitric acid in the gas phase, the highest ammonium nitrate concentrations are observed when there are cooler temperatures (i.e., ammonium nitrate is favored); however, cooler temperatures also minimize the amount of bias or loss of nitrate from the filters. For example, while there is the greatest potential for nitrate losses during the summer months, the fraction of total nitrate (gas plus particle) in the fine particles is much less than in the fall and winter months (Solomon et al., 1988) due to the temperature dependance of the equilibrium of ammonium nitrate with nitric acid and ammonia (Russell et al., 1985). However, loss of nitrate from filters is also less during cooler conditions as found in the fall and winter months. For example, in the winter, in the San Joaquin Valley during IMS95 (Solomon et al., 1996), virtually no loss in ammonia nitrate from Teflon was observed (Watson, DRI, personal communication, 1998).

### **Continuous Measurements**

Continuous methods for the measurement of fine particle mass would have several advantages over the current FRM method. These include: a) not requiring a sequential sampling unit to collect two to seven daily samples per week; b) not requiring both an expensive temperature/humidity-controlled weighing room and extensive labor to weigh the filters; and c) providing short-term (1-hr or less) measurements of fine particle mass concentration. Therefore, even though the capital investment and labor costs are relatively high for the implementation of the fine particle mass standard, little will be learned about the temporal variability of fine particle concentrations, except at a few sites (4-7) that are to be established through the EPA supersites program and through special studies conducted by the states (e.g., California and Texas) and industry (e.g., EPRI southeast study; Saxena, EPRI, personal communication, 1998. This temporal information is needed both for understanding ambient particle health effects and for developing sound mitigation strategies. Finally, the proposed FRM cannot provide the immediate data necessary to calculate the Air Pollution Indices (APIs). Thus, the development of equivalent continuous fine particle methods that will make it possible to obtain richer data sets and to implement cost-effective large monitoring networks.

Currently, there are several continuous instruments available for fine particle measurement, but there are serious reservations regarding the quality of data these instruments can provide. An excellent review is given by Swift (1989). For purposes of this discussion, these continuous monitors can be divided into two categories: a) those which measure properties of the particles while they remain suspended in ambient air (optical/electrical), and b) those which collect particles on a filter or similar fixed substrate.

### Optical/Electrical Methods:

Optical instruments (e.g., mini-RAM instruments, nephelometers, instruments measuring the Coefficient of Haze (COH), etc.) use light absorption or scattering properties to estimate particle mass concentration. These methods are commonly

dependent on both the chemical composition and the size distribution of the particles (Charlson, et al., 1974); some methods are also dependent on temperature and relative humidity. Since particle composition and size vary significantly with time and geographic location, it is difficult to adequately characterize a useful relationship between particle mass and the extinction coefficient. The advantage of these methods is that they do not require the collection of particles on filter media. Interactions between different types of particles collected on the same filter medium and/or particle-to-gas conversions, can result in significant overestimation or underestimation of particulate mass. Obviously, this problem applies both to continuous and integrated methods that collect particles on filter media. Optical and electrical methods are described in Sections A.2.4 and A.7.3. Of those described, the most likely to be used to determine PM mass concentrations employ the differential mobility particle sizer.

Using the DMA and an optical particle counter would make it possible to measure PM mass across a broad size range of atmospheric particles (0.003 - 2.5 \( \mu \) m diameter). Nevertheless, even in this case, the combined optical/electrical counter still would suffer from two major shortcomings. The first shortcoming arises from the fact that these counters measure the number distribution of particles that are subsequently converted to volume distribution. To measure the mass distribution, the particle density needs to be known, which for ambient particles varies with particle composition, both temporally and spatially. However, particle density can be estimated using the epiphaniometer (Gaggeler and Baltensperger, 1989; also see McMurry et al., 1998). The second (and more severe) shortcoming is intrinsic to converting a number to a volume distribution. The number distribution of ambient particles is dominated by ultrafine particles, in the size range 0.01-1.0 \(\mu\)m. The coarser the particles, the smaller their number concentration becomes. However, when converting a number to volume distribution, a 1.0 µm particle weighs as much as 10<sup>3</sup> times a 0.1 µm particle and 10<sup>6</sup> times a 0.01 µm particle. Consequently, this conversion is bound to lead to severe counting errors because a low background concentration of coarse particles, which may just be within the noise of the instrument, will be converted to a significant fraction of the volume distribution. Finally, a serious disadvantage is the very high cost (about \$100,000) of the two combined optical/electrical counter instruments, which is not feasible for use in the national air

quality monitoring network. However, recent work by Ehara et al. (1996) have allowed for the determination of the mass of size-selected particles using a steady-flow mass analyzer (SFMA). Thus, following the DMA or the OPC with a SFMA will allow for the determination of fine particle mass without the above two disadvantages; albeit, the method would still be expensive. Knowing the mass and the size distribution of the particles, it is also possible to determine particle density as a function of particle size (McMurry, 1998a).

#### Filter/Substrate-Based Methods:

There are several filter-based methods for obtaining aerosol mass on a near real-time continuous basis (typically hour averages, but shorter averages can be obtained, however, precision will likely be poorer.) These methods include the beta attenuation monitor, Piezoelectric microbalance, the Tapered Element Oscillating Microbalance, and a method based on pressure drop across a fibrous filter. These methods are described below.

The beta attenuation monitor determines aerosol mass loadings by measuring the change in intensity of beta rays passing through a membrane filter as the particles are being collected on the filter (Macias and Husar, 1976). The intensity of the beta rays passing throught the filter collection medium decreases proportionally with the particle mass loading. A continuous filter tape is used in this automatic sampler, providing a "fresh" filter segment for each measurement. Initially, the beta attenuation is measured through an unexposed filter segment as a blank attenuation. The filter segment then can be exposed to ambient particles for a specified time period for particle accumulation. The beta attenuation measurement is then repeated and the mass concentration is converted after the blank correction (Wedding, 1993). Although this method has the capability, in principle, of reporting hourly average measurements, two- to four-hour averaging periods are needed to obtain enough deposits for accurate measurements at typical ambient particle mass concentrations (Chow, 1995). Also, the relationship between mass and energy absorption depends to some extent on particle composition. In

addition, a radioactive material is required as a source of beta rays adding a potential safety hazard to this method.

The Piezoelectric microbalance, which also collects particles on a substrate, was once considered a perfect way to measure particle mass loadings continuously. Particles are impacted or precipitated onto a piezoelectric quartz crystal disk surface and the decrease of the natural resonate frequency of the quartz disk is directly proportional to the particle mass on the disk, after comparison with a clean reference crystal (Olin and Sem, 1971; Ward, 1990). Although such instruments have been used with some success in providing direct readings of aerosol mass concentrations, they suffer from several limitations. These include saturation effects on the crystal surface, as well as variable particle collection efficiencies. Several investigators (Daley and Lundgren, 1975; Lundgren, 1977) found that the frequency change for a given incremental mass deposit on the sensor does not remain constant as the sensor becomes loaded. This is due to the change in the particle collection patterns over time. Some particles, such as CaCO<sub>3</sub>, deposit uniformly in the beginning but, as the loading increases, the freshly-deposited particles tend to accumulate near the center of the sensor, presumably because of the change in the electrical conductivity of the collection surface. Other types of aerosols, such as Fe<sub>2</sub>O<sub>3</sub>, tend to deposit less uniformly than expected after initial particle deposition on the crystal. As a result, the incremental decrease in frequency of a particle laden crystal is not the same as that of a fresh crystal, causing a potential bias for the particle mass concentration measurement. In the research of Lundgren 1977, the response of the instrument became non-linear within a few minutes after beginning the experiments when tested with black carbon particles.

The Tapered Element Oscillating Microbalance (TEOM) has been widely used as a continuous PM<sub>10</sub> mass measurement monitor (Pataschnick and Rupprecht, 1991) and by replacing the PM<sub>10</sub> inlet with a PM<sub>2.5</sub> inlet has been used to measure PM<sub>2.5</sub> mass concentrations continuously. With this method, particles are continuously collected on a filter mounted on the tip of a glass element that oscillates in an applied electric field. The oscillation frequency of the glass element decreases as the mass of the particles collected on the filter increases. This is a sensitive method with a typical time resolution of five minutes. To maintain the necessary precision, the tapered element must be kept at a

constant temperature to minimize effects of thermal expansion and contraction, and at an elevated temperature to remove adsorbed water, to prevent artifacts due to variation in ambient humidity. For these reasons, the sample chamber and inlet air are normally heated to 50 °C. As a result, there can be significant losses of semi-volatile organic and inorganic constituents, which typically represent a large fraction of the total mass (Allen, et al., 1997). This problem is more pronounced for PM<sub>2.5</sub>, because this size range typically has a greater fraction of unstable compounds (ammonium nitrate and semi-volatile organic compounds) than does PM<sub>10</sub>. In addition, as the composition of the air sample changes, the partitioning of air pollutants between the gas and particle phase changes. Therefore, adsorption and/or desorption of gaseous species can take place on the filter. This gain or loss of mass on the filter is a serious problem, not just with the TEOM, but with any method that collects particles on a filter over a prolonged period of time. To help overcome the problems associated with heating the inlet several groups are working on the design of systems that operate with controlled relative humidity (Rupprecht, 1998; Edgerton, 1998).

Recently, a continuous fine particle mass sampler that can provide 20-minute measurements was developed (Koutrakis et al., 1995). This method is based on the continuous measurement of pressure drop across a fibrous filter (Fluoropore) during particle sampling. The performance of this particle mass monitor has been validated through laboratory and preliminary field tests. A filter tape transportation system allows for unassisted particle sampling for several weeks. For each sampling period, a new segment of the filter tape is exposed. This method combines measurement at ambient temperatures, short sampling periods, and low face velocity, which, together, result in minimum volatilization or adsorption artifacts. In addition, because this technique requires a low flow rate (0.3 liters/min), the relative humidity of the air sample can be controlled to 40% or less by passing the air sample through a Nafion diffusion dryer prior to its collection. This is in accordance with the FRM, which requires that particle filter samples be conditioned prior to weighing at a relative humidity of 40% to remove particle-bound water. These are important features necessary for accurate aerosol measurements relative to the FRM, which are not easily achievable with previous methods. Although this pressure drop method looks promising, more field investigations

are necessary to validate it for ambient air sampling for a variety of geographic locations and seasons (i.e., different chemical atmospheres).

### Summary:

There is a great need for the development of accurate, continuous particle mass monitors. As long as health effects studies cannot identify the chemical constituents or physical properties of particulate matter that are responsible for the observed morbidity and mortality, the total mass of all ambient particle components should be the criterion for particle measurement. Continuous mass monitoring methods need to be robust for both stable species (e.g., sulfates and dust) as well as labile species (e.g., SVOCs, ammonium nitrate and ammonium chloride). Furthermore, the effects of relative humidity and temperature on particle mass measurement also need to be addressed. For example, for comparison to the FRM, sampled particles should be conditioned to 40% RH (when ambient RH exceeds 40%) to minimize the effect of variations in the water associated with particles. The air sample should not be heated because semi-volatile compounds will volatilize, resulting in an underestimation of particle mass. In situ aerosol measurements are necessary to minimize positive or negative particle mass sampling artifacts. If a filter medium is used, the collection surface should not be used for more than one hour to minimize these artifacts. To maintain the gas/particle equilibrium, the continuous method should either regenerate the collection surface or use a new surface for each sampling interval. Finally, none of the existing continuous monitors can provide mass measurements equivalent to those of the FRM. Considering that the ability of the FRM and most of the filter-based methods in general to meet these criteria are questionable (i.e., artifact free mass concentrations), as mentioned above, a serious problem is posed that needs to be addressed in the years to come.

# **A.2.2** Particulate Matter Chemical Composition

This section first describes several methods for determining the chemical composition, and often size of single atmospheric particles. Next, measurement methods

for the determination of specific chemical compounds in bulk time-integrated samples are described, including appropriate laboratory chemical analysis methods. The bulk field collection and laboratory methods are summarized in the critical review by Chow (1995). Continuous chemically specific methods are also described for each species discussed below. The latter, as well as the continuous single particle measurements, represent the state-of-the-science in determining components of atmospheric aerosols.

## Measurements of Single Particles

### Time-Integrated Measurements:

Electron microscopy of single particles collected on grids is the only available technique that can provide particle composition and morphology information simultaneously; although it is not in real-time or continuous (Fletcher and Small, 1993). The combination of scanning electron microscopy and energy analysis of emitted x-rays is the most powerful tool for detailed information about shape and chemistry of single particles. Elemental analysis for elements heavier than sodium is possible. The major limitation of electron microscopy is the extreme amount of labor required to obtain statistically significant data, though semi-automated analysis schemes are available (Anderson et al, 1988; Artaxo et al, 1992). Because high vacuum is conventionally required for analysis, detection of volatile and semi-volatile components is difficult. New techniques have attempted to increase analysis pressure above 5 torr to reduce such losses (Danliatos 1988). Selection of collection grids is also critical, with carbon or copper typically chosen as appropriate to minimize background interference with elements of interest (Huang and Turpin, 1996). Although composition information is labor intensive and often difficult to quantify, the unique combination of morphology and composition make electron microscopy the ideal tool for resolving external mixtures of particles, for example, mixed salt (McInnes et al, 1994) or carbonaceous particles. Collector grids are easy to operate and add to existing sampling protocols.

#### Continuous Measurements:

One of the most significant advances of the last decade has been the development of methods to measure the chemical composition of single particles in-situ in real-time, thus providing important information for characterizing atmospheric aerosols. These methods are summarized in Table A-5. Any chemical/microphysical aerosol model includes external and internal mixtures of particles with complex chemical composition that can only be resolved observationally by detecting single atmospheric particles.

Such atmospheric detection has been demonstrated using laser vaporization of particles larger than about 0.1 to 10 µm diameters (Mckeown et al., 1991; Thomson and Murphy, 1993; Prather et al., 1994; Hinz et al., 1996, Noble and Prather, 1996; Johnston and Wexler, 1995). Particles are detected by laser light scattering which then triggers a high powered UV pulsed laser which vaporizes the particle in a plasma that creates molecular and atomic ions that are then analyzed with a time-of-flight (TOF) mass spectrometer. Sensitivity to trace chemical composition in particles as small as 0.1 µm is very good. The accuracy for chemical speciation is harder to quantify. For example, analysis of organic compounds tends to be equivalent to elemental carbon analysis. Overall, sensitivity is also difficult to quantify since sampling efficiencies are size dependent and not yet well characterized. Efforts to characterize sampling efficiency for the ATOFMS are underway through a study at the University of California, Riverside (Prather, UCR; Cass, Caltech, personal communications, 1998). They are obtaining sizeresolved chemical characterization of aerosols using a MOUDI as well as size distributions by some of the methods discussed above. The size and chemically resolved impactor data provide a calibration measure for the chemical composition data collected by the ATOFMS.

Aerodynamic particle size can be determined by passing particles through two scattering lasers as in the aerodynamic particle sizer (Prather et al., 1994; Noble and Prather, 1996). Other groups have extended measurements to ultrafine particles by randomly firing the vaporization laser (Reents et al., 1995), including using a DMA to size selected particles (Carson et al., 1997). Despite current limitations on accuracy, field observations to date have clearly indicated the potential of such single particle analysis in

Table A-5. Measurements of Particulate Matter Particle (Single Particles Analyzers)

Method	Variable Measured	Limit of Detection	Precision	Accuracy	Potential Interferences/Artifacts	References
Laser Vaporization Mass Spectrometry	size-resolved single particle composition	$0.1 < d < 5 \ \mu m$	fair	poor/fair	sampling bias toward larger particles (>0.5 μm)	Noble et al., 1994; 1996, Prather et al., 1994
Aerosol Mass Spectrometer	size-resolved single particle composition		fair	fair	limited to volatile and semi- volatile components	Jayne et al., 1997

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resolving external mixtures of sulfate and nitrate particles (Murphy and Thomson, 1997), detecting seasalt in sulfate particles aloft (Middlebrook et al., 1997), identifying particle source categories via chemical tracers (Hinz et al., 1996) and tracing the transport of pyrotechnically-derived particles following fireworks (Liu et al., 1997).

A variant of single particle mass spectrometry is an aerosol mass spectrometer (AMS) based on thermal vaporization of single particles (Jayne et al, 1997) sampled with an aerodynamic inlet that focuses particles into a beam coupled to a vacuum chamber (Liu et al., 1995). Following aerodynamic particle sizing using mechanical TOF chopping, particles are vaporized and then detected with a quadrupole molecular mass spectrometer. Particle sizes spanning the range of ultrafine to coarse can be quantitatively analyzed. Although sensitivity is significantly less than for the laser based analyzers and detection is limited to volatile and semi-volatile chemical components, the AMS has the potential to provide a robust, size-resolved real-time aerosol chemical analyzer. AMS instrumentation is based on vacuum and mass spectrometric technology, utilizing no lasers.

The power of single particle analysis has been best demonstrated in the recent study of the conversion of seasalt aerosol from NaCl to NaNO<sub>3</sub> as marine air passed over the Los Angeles coast (Gard et al., 1998). That study represents the paradigm for intensive field programs of aerosol chemistry. While the single particle observations provided the most dramatic evidence for chemical transformation of atmospheric aerosols, overall aerosol microphysics and size/chemical distributions were monitored with a number of ancillary measurement techniques that served to calibrate the single particle measurements.

### Sulfate (and related particle strong acidity)

### *Time-Integrated Measurements:*

Sulfate is one of the most robust species to measure particulate matter because it remains stable during and after sample collection. Most of the existing data are of great accuracy except those collected using glass fiber filters, which have a positive artifact

caused by reaction of the filter material with sulfur dioxide. Sulfate is commonly collected on Teflon or quartz fiber filters (Chow, 1995). Aqueous extracts of these filters have usually been analyzed using ion chromatography (and less frequently, using spectrophotometric methods). In general, sulfate data have an accuracy of about 5%, which is typically independent of the sampling method, location and season. Furthermore, measurements of ammonium ion associated with sulfate, such as ammonium sulfate, letovicite or ammonium bisulfate, have a similar accuracy. Total particulate sulfur also is routinely analyzed using X-Ray fluorescence (XRF). Measurements of collocated samples by ion chromatography and XRF are usually highly correlated. The typical mass ratio of (sulfate by IC)/(sulfur by XRF) is about 3, which indicates that almost all of the fine particle sulfur is in the form of sulfate.

Particle strong acidity (hydrogen ion), is mostly associated with sulfates species. Denuder/filter pack techniques have been used to measure particle acidity and other ionic species (Koutrakis, et al., 1988). The samples consist of three components: a) a PM<sub>2.5</sub> inertial impactor to remove coarse particles (which are generally alkaline and would consequently neutralize the fine particle strong acidity collected on the sample filter); b) a diffusion denuder to remove gaseous ammonia from the air sample; and c) a Teflon filter to collect fine particles. The fine particles are subsequently extracted using an aqueous solution of dilute perchloric acid. The hydrogen ion concentration is measured using a pH meter equipped with a semi-microelectrode. Although the accuracy of hydrogen ion measurements (about 10%) is less than that of the related ionic species, sulfate and ammonium (about 5%), their accuracy is considerably better than those of carbonaceous aerosols and nitrate (about 15%). The ionic balance. [ammonium+hydrogen]/[2x[sulfate]], is close to unity during acid aerosol episodes, confirming the accuracy of the hydrogen ion measurements. Note that during these episodes no significant amount of particle nitrate is present because ammonia has been depleted by reaction with excess acidic sulfate.

#### Continuous Measurements:

Continuous monitoring of particle sulfate is possible using the flame ionization method developed by Huntzicker, et al. (1978). According to this method sulfur species are combusted in a hydrogen flame to create excited sulfur dimers. The intensity of the fluorescence emission is proportional to square of the particulate sulfur concentration. Using a denuder to remove sulfur dioxide and thermal ramping this continuous monitor provides separate measurements of sulfuric acid, ammonium sulfate and bisulfate and, Doping the hydrogen with sulfur hexafluoride improves the non-volatile sulfate. sensitivity and yields a nearly linear response (Appel et al., 1989). An intercomparison between this method and conventional filter samples analyzed by ion chromatography showed good agreement (Suh et al., 1994). Sulfate can also be measured using a chemiluminescence analyzer (Benner and Stedman, 1989). According to this method, particulate sulfur species are converted to SO in a hydrogen flame. Subsequently, SO reacts with O<sub>3</sub> to produce an excited state of SO<sub>2</sub>. Similarly to the flame ionization method, described above, a denuder is used to remove sulfur dioxide. Thermal ramping with this monitor also can provide the same sulfate speciation as the flame ionization method. Finally, it should be mentioned that both continuous methods assume that all particulate sulfur is present in the form of sulfate. This assumption is generally true for typical ambient atmospheres.

Sulfate can also be monitored continuously using annular denuders or wet denuders followed by a steam chamber to form condensation nuclei that are subsequently collected and analyzed in near-real time by ion chromatography. This method can also be used to measure other anions and cations, as well as their gas-phase counterparts (Ito et al., 1998; see the review by Dasgupta, 1993; Simon and Dasgupta, 1995; Wyers et al., 1993).

#### Nitrate

# *Time-Integrated Measurements:*

A variety of filter media have been used to collect particulate nitrates, including: Teflon filters, glass fiber filters, sodium carbonate-coated glass fiber and nylon filters. Aqueous extracts of these filter media were analyzed mostly by ion chromatography or colorimetric methods to determine the nitrate concentration. Accurate measurements of nitrate require the removal of gas phase nitric acid prior to particle collection and the collection of nitrate on a filter medium which binds any nitric acid vapor produced by volatilization of the collected particulate ammonium nitrate, such as sodium carbonatecoated glass fiber or nylon filters. Removal of the gaseous nitric acid can be achieved by using diffusion denuders, typically coated with Na<sub>2</sub>CO<sub>3</sub> or MgO (Koutrakis, et al., 1995; Solomon et al., 1988) or (unanodized) aluminum inlets (John et al., 1988). Previous methods that have used Teflon, glass fiber, or quartz fiber filters are negatively biased due to volatilization of ammonium nitrate during and after sampling (Dunwoody, 1986; Witz, et al., 1990; Solomon et al., 1988; also see Hering et al., 1988 and other related special issue articles). The equilibrium between particle ammonium nitrate, gaseous ammonia and nitric acid can be perturbed by changes in relative humidity and temperatures. Losses of ammonium nitrate can also be caused by the presence of ammonium bisulfate and similar incompletely neutralized forms of sulfuric acid collected on the filter media (Koutrakis et al 1992). To date, there is no agreement among the different studies regarding the extent of nitrate loss. This disagreement stems from the fact that these results correspond to a variety of locations, meteorological conditions, and sampling methods. A recent study by Hering and Cass (submitted to J. Air Waste Manage. Assoc.) presents a model that can be used to estimate nitrate losses. This may become an excellent tool to estimate corrections for particulate nitrate data from previous and future studies.

Nitrate is one of the fine particle constituents that will be measured as part of the fine particle speciation network that the U.S. EPA is planning to initiate. The proposed sampler will be similar to the FRM sampler described above, but will be equipped with a

denuder to remove HNO<sub>3</sub> followed by a nylon filter to collect fine particle nitrate free from artifacts. Nylon filters are slightly alkaline and can collect nitrate quantitatively. However, there is some evidence that a small amount of nitrogen dioxide can be collected by these filters (Preliminary results obtained during the Harvard/EPRI methods validation studies). A small fraction of ambient nitrogen dioxide is initially retained in the form of nitrite and is converted slowly to nitrate by ozone or other atmospheric oxidants that are present in the air sample. This positive bias may be about 5-15% at sites with high nitrogen dioxide concentrations. Future studies are needed to investigate this artifact.

Nitrate, as well as other semi-volatile compounds, can be lost after sampling during shipping and storage. Witz et al. (1990) found that a large fraction of nitrate and ammonium (greater than 50%) was lost from glass- and quartz-fiber filters that were stored in unsealed containers. These containers were stored for a period of two to four weeks prior to analysis. Therefore, the use of sealed containers maintained at reduced temperatures during shipping and storage is necessary to minimize these losses.

#### Continuous Measurements:

The Automated Nitrate Monitor is a new method that provides automated measurement of airborne particle nitrate concentrations with a time resolution of ten minutes (Hering and Stolzenburg, 1998). The method uses an integrated collection and vaporization cell whereby particles are collected by a humidified impaction process, and analyzed in place by flash vaporization. The system operates continuously, unattended, yielding 144 measurements per day, each corresponding to an eight-minute sample collection followed by a 90-sec analysis. Operations are unattended apart from twice-weekly calibration checks. Preliminary results are available immediately.

The approach is similar to the manual method that has been used for over twenty years to measure the size distribution of sulfate aerosols (Hering and Friedlander, 1982). In this case, however, the particle collection and analysis have been combined into a single cell, allowing the system to be automated. Particles are humidified prior to impaction to eliminate the rebound of particles from the impaction surface without the use of grease (Winkler, 1974; Stein et al., 1994). Interference from vapors such as nitric

acid is minimized by use of a denuder upstream of the humidifier. Analysis is done by flash-vaporization into a nitrogen carrier gas with quantitation by a chemiluminescence  $NO_X$  analyzer, similar to that described by Yamamota and Kousaka (1992) and described in Section A.1.1 of this report. The flow system is configured such that there are no valves on the aerosol sampling line. Field validation procedures include on-line checks of particle collection efficiency, calibration with aqueous standards applied directly to the collection substrate, and determination of blanks by measurements of filtered, ambient air.

The method has been compared to 10-min data for total fine particle concentrations as indicated by nephelometry, and to 6 to 24 hour nitrate concentrations measured by denuded filter methods. For measurements in Denver Colorado (NFRAQS) and in Riverside (SCOS'97) the 10-minute changes in fine particle nitrate tracked the 10-minute changes in particle scattering. For the initial measurements in Denver, some discrepancies were found with the filter measurements. However, for Riverside, comparison with 14 days of 24-hr denuder-filter sampling gives a correlation coefficient squared of R<sup>2</sup>=0.87, and shows no significant bias (i.e., the regression slope is not significantly different from 1) (Saxena, private communication, 1998). As currently configured, the system has a detection limit of 0.7 µg/m³, and a precision of 0.2 µg/m³. Field operations with the system in Riverside showed that it was robust, providing nearly uninterrupted data over the six-week study period.

As described under sulfate, particle nitrate also can be determined continuously, in near-real time using a combination of annular or wet denuders coupled to an ion chromatographic system.

#### Ammonium

## *Time- Integrated Methods:*

Particles collected on Teflon filters are extracted using an aqueous solution. Ammonium ion can be analyzed using ion chromatography (IC) or colorimetric methods. Although ion chromatography is more expensive and more labor intensive, it has become

the method of choice, because of its versatility and accuracy. For instance, ion chromatography can be used to measure other important cations, such as sodium and potassium and anions such as nitrate, sulfate and chloride; although separate IC columns are needed to measure both cations and anions. Colorimetric methods can only measure one species at a time. Because ammonium sulfate salts are very stable, negligible loss occurs during sample collection and storage. However, ammonium nitrate, which is an important constituent of fine particle mass, is unstable and can volatilize during both sample collection and storage. The extent of volatilization depends on many parameters, including temperature and relative humidity. The dissociation of ammonium nitrate results in the formation of gas phase ammonia and nitric acid. As mentioned above, a nylon membrane or sodium carbonate-coated filter is used to trap the nitric acid lost from the Teflon filter. Since no collection medium is used for the volatilized ammonia, one would expect that current sampling techniques underestimate ammonium concentrations due to volatilization of ammonium nitrate. It is worth mentioning that fine particle mass contains many acidic compounds. Consequently, a fraction of volatilized ammonium (in the form of ammonia gas) can be retained on the Teflon filter by reacting with the acidic compounds; however, this has never been quantified. This mechanism can reduce underestimation of collected ammonium ion caused by volatilization.

### Continuous Measurements:

A semi-continuous measurement method was recently developed by Ito et al, 1998. According to this method particles are collected in a small mist chamber. Similar methods have been used for the measurement of related acidic gas-phase and particle species (see the review by Dasgupta, 1993; Simon and Dasgupta, 1995; and discussed previously under sulfate). Subsequently, the dissolved ionic species (including ammonium) are analyzed by an on-line ion chromatograph. This method can provide short-term measurements (thirty to sixty minutes). While the method is accurate and sensitive, the instrument is bulky and requires wet chemistry in the field.

### Chloride

Time-Integrated Methods and Continuous Measurements:

Aqueous extracts of Teflon filters can be analyzed using ion chromatography to determine chloride concentrations as described above under continuous methods for ammonium. Although chloride can be an important constituent of fine particulate matter in coastal environments, to date only a few studies have measured this species (see for example, Solomon et al., 1988a; 1989; Eldering et al., 1991). One reason for this is that many precautions must be taken during filter preparation, sampling, transport and analysis to minimize chloride contamination of the samples. High and variable blanks for both laboratory and field can cause sample values to be merely qualitative. A method to continuously measure chloride has not been reported to date, however, the continuous denuder/IC methods described above for sulfate and ammonium could be used for chloride measurements, if appropriate precautions are made to assure that blank values are low.

### Elements

## *Time-Integrated Measurements:*

Elemental analysis of aerosol samples is important because it can be helpful in identifying particle sources. To date several analytical methods have been used to determine the elemental composition the particulate matter. These methods include: of X-Ray Fluorescence (XRF), Proton Induced X-Ray Emission (PIXE), Instrumental Neutron Activation Analysis (INAA), Atomic Emission Spectrophotometry (AES), Inductively Coupled Plasma (ICP) equipped with atomic emission (ICP-AES) or mass spectroscopy (ICP-MS). From these methods XRF and PIXE are the most widely used because they require no sample preparation. In contrast, both AES and ICP methods require filter extraction of the filter sample using strong acidic solutions to achieve sample dissolution. However, because ambient particles are complex it is difficult to

dissolve them completely, regardless the strength of the solvent, thus reducing the accuracy of the analysis. Also, extraction is a time consuming and expensive. Nonetheless, AES is used occasionally for the analysis of sodium and magnesium, which cannot be analyzed by either XRF or PIXE methods. ICP-AES and ICP-MS can be used to analyze a large spectrum of elements with detection limits suitable for aerosol samples. However, as with AES, these methods require sample extraction and are destructive. ICP-MS can also be used for isotope analysis. Although INAA is a non destructive method, the sample must be folded and sealed in plastic. Because the sample is bombarded by gamma rays it becomes radioactive. Of course this makes it difficult to use the sample for further analysis. Finally, INAA cannot be used for the analysis of certain important elements, including sulfur, lead, and silicon; however, it is extremely sensitive for many trace metals, especially the rare earth elements.

XRF (Dzubay and Stevens, 1975; Jaklevic et al., 1977) and PIXE (Cahill et al., 1990) have been used extensively in the analysis of ambient aerosols because they are non-destructive, have multi-element capabilities, and have relatively low cost. These methods are usually performed on Teflon filters for approximately forty elements (from sodium to uranium). However, for typical atmospheres the analysis is meaningful only for half of these elements, including aluminum, silicon, sulfur, chlorine, potassium, calcium, titanium, vanadium, chromium, manganese, iron, nickel, copper, zinc, arsenic, selenium, bromine, cadmium, and lead. The sensitivity of these methods is on the order of few ng/m<sup>3</sup> for twenty four-hour samples (flow rates of 10-20 liters per minute). Because these detection limits are quite low, XRF and PIXE analysis provide meaningful information for typical samples. Nonetheless, quite often environmental samples have elemental measurements that are below the detection limit of the methods. Thus analytical uncertainties can have a significant impact on the quality of the data analysis such as for source apportionment studies. Since particle concentrations are expected to decrease due to the implementation of the new PM NAAQS, XRF and PIXE may not be sensitive enough. Finally, it should be mentioned that during the analysis using these methods, the sample is introduced into a chamber that is evacuated and the sample is slightly heated due to the absorption of X-rays or protons. As a result, species that can volatilize such as ammonium nitrate and certain organic compounds can be lost during

the analysis. This is overcome, however, by using atmospheric pressure energy dispersive XRF using secondary ions as the excitation source. In these systems, air is replaced with He while maintaining atmospheric pressure, and sample heating by direct X-ray methods is eliminated due to the use of secondary ions as the excitation source.

#### Continuous Measurements:

To date there are no continuous measurement techniques for the quantitative elemental analysis of ambient aerosols. Currently, some research efforts are under way, (Ondov, University of Maryland, personal communication, 1998), but it will take at least one to three years before new monitoring techniques will appear. These techniques will be useful for generating the quality of data sets needed for more comprehensive source apportionment studies.

## Carbonaceous Compounds

## *Time-Integrated Measurements:*

There are three types of carbonaceous particles:

Organic carbon that can be present in the form of hundreds (or more) of organic compounds such as alkanes, alkenes, mono and di-carboxylic acids, aromatic polycarboxylic acids, polyaromatic hydrocarbons, ketones, quinones, nitrogen containing compounds, etc. These compounds do not absorb light in the visible region, and a large fraction of them can be present in both the particle and gaseous phases (semi-volatile species).

Elemental carbon or (visible) light absorbing carbon.

Carbonate carbon, which is in the form of calcium carbonate or other salts.

Several methods have been employed to separate or measure independently the concentrations of elemental carbon and organic carbon in atmospheric particles: thermal analysis, digestion, extraction, optical methods, photoacoustic methods. Of these, thermal analysis, optical methods, and photoacoustic spectroscopy are used most often today. These methods are discussed in detail by Wolff and Klimisch (1982), Cadle et al. (1983), and Yasa et al. (1979).

The collection of carbonaceous particles is still an area of considerable controversy. One simple method that has been widely used is to collect total carbon on a series of two quartz filters. Presumably, the first collects all of the particle phase carbon (elemental and organic) and a small fraction of gas-phase organic carbon. Likewise, the second quartz filter is supposed to collect only the same small fraction of gas-phase organic carbon as collected by the first filter. Therefore, the concentration or particle phase organic carbon is calculated by subtracting the amount of organic carbon on the second from that on the first stage. However, this assumption does not take into account particle phase organic carbon that can volatilize from the first filter and be collected by the second quartz filter. When this volatilization occurs, it results in underestimation of particle phase organic carbon, similar to the situation with the collection of particulate ammonium and nitrate on filters described above.

The two-quartz filter approach has been used by the IMPROVE network for the determination of organic and elemental carbon. Because the accuracy of this method is questionable, as described above, more research is needed prior to its implementation. Eatough et al. (1989) and Tang et al. (1994) concluded that desorption of organic gases from particles on the first quartz filter was the dominant sampling artifact (negative artifact), while Turpin et al. (1994) suggested that organic gases can be collected by the quartz filter (positive artifact). Turpin et al. found that adsorbed organic gases represent 10 to 40% of the organic carbon measured on quartz filters in southern California. This study suggested that: a) organic gas absorption (positive bias) was much larger than organic particle volatilization (negative bias); b) as sample durations increase the fraction of the adsorption bias decreases because the adsorbed gases reach equilibrium with the collected particles and the filter becomes saturated; and c) the magnitude of the bias depends on the composition of the organic gases and particles present in the air sample.

For these reasons, the US EPA national speciation network is suggesting the use of denuders (carbon or XAD-2 coated) to remove semi-volatile organic species and reactive organic gases that might absorb on a quartz filter (EPA, 1998). However, additional testing and evaluation of the denuder/filter method system is needed (Turpin, 1998).

There is a great need to develop bias-free particle organic carbon sampling techniques. The diffusion denuder approach may be a sound approach to overcome the problems mentioned above. According to this sampling technique, gaseous organic compounds are removed using an activated carbon diffusion denuder or an XAD-2 coated denuder. Subsequently, the particle-phase organic carbon can be collected downstream of the denuder using a series of two-quartz filters or a quartz filter followed by a PUF cartridge. The first filter collects particle phase organic carbon, while the second quartz filter or PUF cartridge collects the organic carbon volatilized from the first quartz filter. The total particle carbon concentration is determined by adding the concentrations of the first and second filter or PUF cartridge, respectively. To achieve maximum accuracy, the denuder must collect close to 100% of all gas phase organic compounds, and the second filter must collect all of the volatilized organics coming off of the first filter. Multichannel activated carbon denuder or XAD-coated denuder systems also have great potential, but they need to be developed and tested further.

Elemental carbon can be determined by optical methods, by thermal analysis, and by photoacoustic spectroscopy. Optically, elemental carbon is determined by measuring the absorption or reduction in transmittence of light passed through a particle-laden Teflon or quartz filter, such as in the integrating plate method (Lin et al., 1973). Today, thermal methods, which use temperature to separate organic carbon from elemental carbon, are combined with optical methods, where either light reflectance (TOR), or light transmission (or absorption, TOA) is measured and used to compensate for charring of organic carbon during the last thermal OC temperature step. However, their results differ depending upon the specific organic composition of the collected particles. All thermal methods measure carbon (usually as methane) and thus have to multiply the carbon concentration by an average factor of 1.4 to estimate total organic compound mass concentrations. This factor comes from an old study and is expected to vary with location and season and usually may be higher than 1.4 as discussed by Andrews et al.

(1998). Therefore, organic compound concentrations may be higher than those reported by previous studies. Photoacoustic spectroscopy deduces the elemental carbon concentration from light absorption by measuring the sound generated due to heating of the sample by laser light (Adams et al., 1990; Turpin et al., 1990a; Arnott et al., 1998b). Good agreement has been shown (within 15%) between a light absorption filter technique and photoacoustic spectroscopy (Foot and Kilsby, 1989) and the thermal-optical method and photoacoustic spectroscopy (Turpin et al., 1990). All three methods for determining elemental carbon are described in more detail below under continuous methods.

Organic compounds can represent a large fraction of fine particle mass (e.g., Gray et al., 1984; Solomon et al., 1986; 1989). Also organic compound speciation can provide a great deal of information regarding the sources and formation processes of carbonaceous particles (Schauer et al., 1996). Although speciation is desirable, it is not easy to perform because there is no single analytical method that can be used to analyze Usually, non-polar organics are analyzed using thermal all classes of organics. desorption or solvent extraction followed by gas chromatography (GC) and mass spectrometry (MS) (Mazurek et al., 1987; Mazurek et al., 1993; Schauer et al., 1996). Analysis of polar organic compounds is more challenging because special sample preparation is required (e.g. derivatization) for the different compound classes (Blando et al., 1998). Comprehensive determination of organic speciation is expensive and yields a large data set that may be time consuming to process and incorporate into air quality models. It may be more cost-effective to develop inexpensive methods that allow the measurement of specific characteristic groups of organic compounds (Turpin, 1998). Similar lumping approaches for VOC species have been used successfully in ozone modeling. Attempting to obtain a comprehensive spatial and temporal patterns on hundreds of organic compounds may not be a sound strategy. On the other hand, organic aerosol speciation has provided an extensive new set of tracers for receptor-type modeling and has allowed for the apportionment of many more sources to PM at receptors than would occur using just the major species and existing inorganic tracers (e.g., lead is no longer a suitable tracer for automobiles) (Schauer et al., 1996 and references within).

#### Continuous Measurements:

Elemental carbon (EC) concentrations can be estimated from light absorption measurements and photoacoustic spectroscopy. The aethalometer is the most commonly used instrument (Hansen and Rosen, 1990) for determining light absorption of atmospheric particles. In this method, particles are continuously collected on a quartz-fiber filter tape. The difference in light absorption between the exposed and blank sections of the tape is assumed to be proportional to the amount of the light-absorbing particles. It is also assumed that all light absorbing material is elemental carbon and that its light absorption coefficient remains constant for different sources. However, this assumption has not yet been thoroughly validated. A few studies have shown a good agreement between aethalometer data and thermal analysis methods (Allen et al., 1997). However, more studies need to be conducted to examine the relationship of light absorption vs elemental carbon as a function of ambient aerosol composition.

An *in-situ* thermal/optical carbon analyzer has been developed by Turpin and Huntzicker (1991). In this method, particles are collected on a quartz-fiber filter. Organic carbon is then volatilized by heating the filter at 650°C in a helium atmosphere. This volatilized organic carbon is then converted to carbon dioxide, which is subsequently reduced to methane, which is measured using a flame ionization detector as mentioned earlier. Elemental carbon is measured by lowering the temperature to 350°C in the presence of oxygen. The evolved carbon dioxide is reduced to methane and is measured by the flame ionization detector. During volatilization of the organic carbon, light transmission through the filter is measured to make a correction for charring that is caused by pyrolysis of the high temperature organic species. Finally, an identical quartz filter is placed downstream in order to take account collection of gas phase organic carbon by the first quartz filter.

A continuous organic/elemental carbon has been developed (Turpin et al., 1990) and a similar instrument is available commercially. In these methods, aerosol is either collected on a filter (Turpin et al., 1990) or particles are collected on an impaction surface (Rupprecht & Patashnick). Subsequently, the surface is heated at two different temperatures in order to measure the concentration of organic and elemental carbon.

Although this method can provide information about the temporal variability of carbon concentrations, the accuracy is questionable for two reasons: a) they only collect particles above 0.15 µm, which can result in a negative bias because a large fraction of particles containing carbon can have a diameter below this size; and b) during the thermal ramping organic carbon can be pyrolized, which can result in a negative bias for organic carbon and in a positive bias for elemental carbon. Unlike the thermal optical method, charring is not corrected and the extent of these biases will depend on the composition of the carbonaceous particles.

Photoacoustic spectroscopy is based on the photoacoustic effect (Pao, 1977; Rosencwaig, 1980). In this method, radiation from a laser beam is absorbed by the sample and transferred as heat energy to the surrounding gas, which creates an increase in pressure in the sample cell. By modulating the laser, the oscillating pressure forms a sound wave that is detected with a microphone. The microphone signal is directly proportional to the optical absorption. The lower limit of detection for light absorption is  $0.4 \text{ Mm}^{-1}$ , which corresponds to an elemental carbon mass density of about  $40 \text{ ng/m}^3$ , assuming a light absorbing efficiency of  $10 \text{ m}^2/\text{g}$ . A comparison of the photoacoustic method to the thermal/optical method has been performed (Turpin et al., 1990a and references within; Adams et al. 1990). The two methods compared well with  $R^2$ =0.82 and a slope statistically equal to 1. Recently, Arnott et al. (1998a) compared photoacoustic measurements of aerosol light absorption with concentrations of black and elemental carbon and obtained strong correlations ( $R^2$  = 0.94 and 0.85, respectively).

### A.2.3 Gas-Phase Condensable Chemical Species

## Nitric Acid and Ammonia

## *Time-Integrated Methods*

Nitric and ammonia gases are precursors of important fine particle mass constituents such as nitrate and ammonium, respectively. Therefore, determination of the ambient concentration of these gases is important. Although different types of integrated

active and passive sampling techniques exist for these gases, the most important are those that use diffusion denuders. Denuder based sampling techniques are accurate, sensitive and relatively easy to use. Tubular, annular, honeycomb glass, or cloth denuders can be coated with sodium carbonate or citric acid to collect nitric acid or ammonia, respectively. After sampling, the denuders are extracted using an aqueous solution. Subsequently, the extract is analyzed by ion chromatography for nitrate or ammonium to determine the nitric acid or ammonia concentration, respectively. For collection rates ranging between 10 and 20 liters per minute and sample durations of twenty four hours the detection limits for these methods are on the order of 1ppb (Koutrakis et al., 1988).

Denuder methods coupled to ion chromatography have been reported to measure HNO<sub>3</sub> and NH<sub>3</sub> continuously in-situ and are also capable of determining aerosol nitrate and ammonium (Dasgupta, 1993; Jongejan et al., 1997; Simon et al., 1991; Lindgren, 1992; Vecera and Dasgupta, 1991; Sorensen et al., 1994). These methods show great promise for continuous, near real-time measurements of HNO<sub>3</sub>, HCl, HNO<sub>2</sub>, and SO<sub>2</sub>, and their particulate phase counterparts. These systems have also been used aboard aircraft platforms (Dasgupta and Lindgren, 1989; Kok et al., 1990). However, whether used at ground-level or aboard aircraft, more thorough evaluations of these methods are needed.

A second denuder-based method uses tubular or annular denuders coated with MgO to remove acidic gases with great efficiency and capacity. Since the MgO denuder cannot be analyzed directly for the acidic gases of interest, a second reactive filter is located in parallel to collect both acidic gases and their aerosol counterparts. The difference between the two reactive filters is the gas-phase concentration of the acid species of interest (see, for example, Solomon et al., 1988; Hering et al., 1988). This method is usually referred to as the denuder difference method. The reactive backup filter, typically, is pre-washed nylon when using a MgO coated denuder; however, fibrous filters impregnated with Na<sub>2</sub>CO<sub>3</sub> or KOH can also be used, but then the denuder should be coated with these bases to provide consistency with the reactive filters. Nylon is best used only for HNO<sub>3</sub> due to variable blanks for chloride and variable reactivity for NO<sub>2</sub> and SO<sub>2</sub> that can result in positive artifacts for nitrite and sulfate. The denuder difference method performed best of the methods tested, relative to an FTIR, for the

measurement of HNO<sub>3</sub> during the Nitrogen Methods Species Comparison Study (Hering et al.; 1988).

## Hydrochloric Acid (HCl)

As mentioned in Section A.1.5, HCl concentrations in ambient air can be obtained continuously by TDLAS and by time-integrated measurements using filters and diffusion denuders. Collection of HCl by denuders can be done either by extracting the denuder coating and analyzing it directly for the concentration of the gas-phase species that have been collected on the denuder coating or by the denuder difference method (Solomon et al., 1988a, 1998b; Eldering et al., 1991). These are the same as the denuder methods for collecting HNO<sub>3</sub> and aerosol nitrate (Hering et al., 1988 and references cited therein; Solomon et al., 1988). In the first method, HCl is collected on a basic coating (e.g., Na<sub>2</sub>CO<sub>3</sub>, KOH) applied to the denuder surface, extracted, and analyzed as chloride ion, e.g., by ion chromatography. As described above for HNO<sub>3</sub> and NH<sub>3</sub> and their aerosol counterparts, continuous methods using denuders coupled to ion chromatography are also capable of measuring HCl in near real-time.

In the second method, as described above for HNO<sub>3</sub> and NH<sub>3</sub>, the sampled air is split between a denuder-filter pack configuration (DF) and a filter pack (FP) only configuration. The filter in both configurations is a reactive filter that acts as a perfect sink for HCl (e.g., Na<sub>2</sub>CO<sub>3</sub>, KOH, pre-washed nylon), not allowing particulate chloride to volatilize. The denuder is also coated with a basic material (e.g., Na<sub>2</sub>CO<sub>3</sub>, KOH, MgO) that removes the acidic gases, including HCl. Gases are collected in the denuder and only particles are collected by the filter in the DF configuration. Both HCl and particulate chloride are collected on the filter in the FP configuration. The difference between the chloride ion measured on the two filters provides an estimate of gaseous HCl. The denuder difference method, using MgO coated denuders and KOH impregnated filters was used to examine the reaction of HNO<sub>3</sub> with sea salt particles (NaCl) producing HCl and coarse particle NaNO<sub>3</sub> in the Los Angeles air basin (Eldering et al., 1991). The denuder difference method also is suitable for measuring ammonia in air. In this case, the denuder and reactive backup filters are coated and impregnated,

respectively with citric acid. In fact, formate and aldehyde can be determined in this same manner using KOH as the reactive base (Solomon et al., 1998a); although PAN might interfere with the acetate measurement.

#### Continous Methods:

Spectroscopic methods have been described earlier (see Section A.1.1). As described earlier for the measurement of sulfate and ammonium, HCl can be measured continuously using wet denuders coupled to an ion chomatograph.

### A.2.4 Particle Number and Size Distribution

Physical properties of atmospheric particles, such as number concentration and size distribution, have been recently reviewed by McMurry (1998) for the 1998 NARSTO (North American Research Strategy for Troposheric Ozone) Scientific Assessment of ozone-related science. A summary of some of the methods is given Table A-6. McMurry's critical review addresses methods for the measurement of particle physical properties and particle chemical composition. This section addresses only the measurement of physical properties of the particles, including total number concentration, cloud condensation nuclei concentration, and size-resolved measurements. In his review, McMurry provides a summary of measurement methods related to each property of the particle and discusses factors that affect measurement uncertainty for each individual measurement methods. Quantifying uncertainty with these measurements is problematic and depends on many assumptions, which are too lengthy to describe here. Therefore, we provide here only a brief summary of the methods and issues affecting their uncertainty and are providing only qualitative estimates of precision and accuracy in Table A-6. Readers are referred to McMurry (1998) for additional details.

Many of the instruments or methods indicated below have been used aboard aircraft and several have been intercompared aboard aircraft. However, problems result due to differences in sampling flow rates at the inlet and inlet transfer tubes versus the speed of the aircraft, which occurs even with isokinetic sampling inlets, due to

Table A-6. Measurements of Particulate Matter (Size Distribution and Related Particle Properties)

Method	Variable Measured	Limit  Detection	<u>Precis</u> <u>ion</u>	Accuracy	Potential Interferences/Artifacts	References
Particle Counting/Sizing						
Optical Particle Counter/Sizer	Particle size via optical scattering amplitude	< 1 particle cm-3 0.1 < d < 50 um	Poor	Poor	Sensitive to particle shape, refractive index	Dick et al., 1994 Baumgardner, 1998
Aerodynamic Particle Sizer	Aerodynamic particle diameter				Sensitive to particle shape, density	Wilson and Liu, 1980
Condensation Nuclei Counter (CNC)	Density of nucleated particles	< 1 particle cm-3 d > 0.01 um	Excellent	Excellent	No size resolution Sensitive to small particles	Stolzenberg and McMurry, 1991
Differential Mobility Analyzer (DMA/CNDC)	Density of submicron particles	< 1 particle cm-3 0.01 < d < 1 um	Excellent	Good	Multiple charging for particles > 0.1 um	Wang, Flagan, 1990 Russel et al., 1996
Electrical Aerosol Analyzer	Density of submicron particles	< ? particle cm-3 d > 0.01 um	Good	Good	Multiple charging for particles > 0.1 um	Winklmayr et al., 1991

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environmental changes during sampling, such as changes in temperature and pressure, and due to compression as gases and particles slow down in the sampling inlet (see Section A.8 for additional details regarding sampling aloft from aircraft platforms. Other uncertainties due to sampling aboard aircraft are summarized in McMurry (1998 and references cited therein).

### **Number Concentration**

Particles, in the less than about 0.1 µm size range (ultrafine particles) act as condensation nuclei for the formation of larger particles. The total number concentration of particles that act as condensation nuclei are determined by condensation nucleus counters (CNC). In this method, particles are grown by condensation of a liquid to the particle surface as particles pass through a supersaturated liquid, with growth factors of 100 to 1000. CNCs can detect individual particles as small as 0.003 µm (3 nm); although this depends on instrument design and sampling pressure and for particles less than about 0.05 µm on the size and composition of the particles (see McMurry, 1998 and references therein; Liu and Pui, 1974a). The upper size limit is about 0.5 µm (Finlayson-Pitts and Pitts, 1986). The most common condensing vapors used in CNC are water and n-buty alcohol. The original particle represents only a small fraction of the total particle after growth so factors such as particle shape and chemistry do not affect detection.

The CNC instruments in use today develops condensation to the particles based on steady-flow, forced-convection heat transfer. In this method, supersaturation is achieved by heat transfer from the warm aerosol (35-40 °C) to the wall of the condenser (~10 °C) as the particles pass through a laminar flow condenser (Sinclair and Hoopes, 1975; Bricard et al., 1976). Two detection methods are employed in CNC counters: direct or single particle counting instruments and indirect detection instruments. Direct detection instruments determine particle concentrations by counting individual saturated particles. Uncertainties for single particle counting instruments are determined primarily by uncertainties in aerosol sampling rate, Poisson counting statistics, and minimum detectable size. Indirect measurement of particle number concentration is achieved by measuring light attenuation through or the light scattered by multiple droplets. These

instruments require calibration with an independent standard that can deliver known concentrations of particles. Currently, indirect-counting CNC instruments are calibrated using the differential mobility analyzer (DMA) that introduces into the CNC singly-charged, monodisperse particles selected from a polydisperse aerosol of know composition by electrostatic classification (Liu and Pui, 1974a). Uncertainties with indirect counting instruments depend on the accuracy of the calibration, instrument stability, signal-to-noise ratio, minimum detectable size, and sampling line losses. Typically accuracies of about 10% are obtained; although in the presence of high concentrations of nanoparticles larger uncertainties are observed (McMurry, 1998).

## Cloud Condensation Nuclei Concentrations

Cloud condensation nuclei (CCN) counters measure the concentration of particles converted to cloud droplets by condensation of water at a specified supersaturation. This information is important for understanding chemical processing in cloud and fog droplets and the effect of clouds and fogs on the atmospheric radiation budget. Since saturation in clouds, occurs at water vapor supersaturations just over 100%, CCN counters operate at supersaturations of about 0.01 to 1% and only use water as the condensing liquid. Because of these lower saturation concentrations of the condensing fluid, the number of particles saturated and detected by the CCN is much lower than that with the CNC, which operates at several hundred percent supersaturation. Design parameters for CCN counters include the range of saturation ratios employed, the method used for determining the relationship between CCN concentrations and saturation ratio, and the particle growth time (e.g., 100 s for CCN at low supersaturations relative to the CNC counter that operates at 0.3 s) (McMurry, 1998).

A number of different approaches used in CCN instruments are described in McMurry (1998) and in a review of CCN instruments by Hudson (1993) and will not be repeated here. Differences in the methods relate to the design parameters mentioned above. The approaches summarized by McMurry include isothermal haze chambers (IHC), static thermal gradient diffusion cloud chambers, and continuous flow diffusion cloud chambers. Several instruments have been designed for use aboard aircraft and they

are summarized in McMurry (1998) as well. Three workshops have been held to compare the performance of various CCN counters. The three workshops were held in 1967, 1970, and 1980, the latter being the most comprehensive one (Journal de Recherches Atmospheriques, 1981, pages 181-373). Results from this third workshop indicate agreement among the same methods ranging from as good as 40% among the IHC methods to as good as 15% among the other methods. Only the same methods can be compared as each method uses different design parameters and essentially measures difference size ranges of particles.

## Size-Resolved Measurements

Several methods are available for measuring size distributions of particles in the atmosphere based on the different properties of the particles. These include sizing particles based on optical properties, aerodynamic size, electrical mobility, diffusion characteristics, and condensation relationships, the latter being discussed above with regards to number concentration. However, because these methods differ in the property of the particle they are measuring, different sizes can be reported for the same particle. For example, as summarized by McMurry (1998), the aerodynamic size obtained with impactors or other aerodynamic particle sizers depends on particle shape, density, and size, while electrostatic classification depends on particle shape and size, but not density, and optical sizes depend on particle refractive index, shape, and size. These sizes can be different from the geometric or Stokes sizes that would be observed in a microscope. However, converting from one measure of size to another can be done; although it may result in significant uncertainty (e.g., see Sloane, 1984; McMurry et al., 1996). For additional details on the methods described below, the reader is referred to McMurry (1998) and Finlayson-Pitts and Pitts (1986).

Impactors have been used to determine discrete size fractions of ambient aerosols, sized by aerodynamic diameter, in the size range from about  $0.05-30~\mu m$ . Operating impactors at reduced pressures has extended the lower size range down to below  $0.05~\mu m$  (Hering et al. 1978, 1979). Impactors operate by accelerating particles through an acceleration nozzle, which gives particles greater than a certain size sufficient momentum

to impact on a collection substrate, while smaller particles follow the air stream around the collector to either another, smaller acceleration nozzle-collection substrate pair or to a backup filter. The backup filter collects all particles less than the final collection surface. Several impactors are described by Finlayson-Pitts and Pitts (1986). Impactors have been designed with only one acceleration nozzle-collection substrate pair, while others may have up to 10 pairs, thus fractionating the aerosol into 10 size ranges. Real impactors employ a solid collection substrate (e.g., aluminum), while virtual impactors use a collection cone. Therefore, virtual impactors use still air as a virtual impactors useful air as a virtual impactor, while smaller particles flow around the cone and are collected separately from the larger particles. Virtual impactors do not suffer from particle bounce problems associated with real impactors; however, their cutpoint (i.e., the shape of the collection efficiency curve) is not as sharp as real impactors. For real impactors, the particle bounce can be minimized by conducting the measurements at a relative humidity in the range of 70 to 80% (Stein et al., 1994; Sorenson and McMurry, 1998; Vasiliou et al., 1998).

Light and electron microscopes can be used to determine particle sizes in the range from about 0.4 to 100 µm and about 0.001 µm or larger, respectively. These methods require collecting a small sample on a smooth flat surface and then counting and measuring the particles manually or by computer processing. This is a labor intensive method and is typically only used in conjunction with determining particle morphology or single particle chemical composition by scanning electron microscopy (SEM) where the electron beam causes the sample to emit fluorescent X-rays characteristic of the elements present in the sample. Thus, SEM allows for determination of chemical composition of individual particles.

Optical particle counters (OPC) measure the amount of light scattered by individual particles as they move across a focused beam of light. The scattered light is collected and converted into a proportional voltage pulse. Particle size is determined from the magnitude of this voltage using a calibration curve obtained using spherical particles of known size and composition. A review on the theory of optical aerosol behavior and its application to particle measurement is given in Willeke and Liu (1976). Gebhart (1993) reviews aerosol measurements by light scattering. OPC use either

incandescent (white) or monochromatic (lasers) light as their light source. White light OPC typically have minimum detection limits of about 0.3  $\mu$ m, while laser OPC have minimum detection limits of about 0.05  $\mu$ m due to their higher illuminating intensity. Thus, laser OPC are more desirable for particles smaller that the wavelength of the illuminating light, while white light OPC are more advantageous for larger particles. In general, OPC measure particles in the size range from about 0.01  $\mu$ m to about 10  $\mu$ m.

Determination of particle size from OPC response can be calculated form Mie theory and the refractive index of the measured particles. Uncertainties in the determination of size distributions result from not knowing the refractive index, shape, or morphology of the measured particles. To help reduce these uncertainties, Hering and McMurry (1991) calibrated the OPC with atmospheric aerosols of known size. They used an electrical classifier to determine particle size prior to delivering the particles to the OPC. Other particle properties (estimates of particle shape and/or refractive index) that can be derived from an OPC are summarized in McMurry (1998). Whitby and Willeke (1979) describe potential problems associated with optical particle counters and discuss ways to minimize the problems.

Aerodynamic particle size is inferred from particle velocity determined by the time-of-flight between two points separated by a known distance (Dahneke, 1973; Mazumder et al., 1991). At least three commercial instruments are available (Baron et al., 1993). The aerodynamic diameter is defined as the diameter of a unit density sphere that has the same settling velocity as the particle (Hinds, 1982), where settling velocity is the difference between aerodynamic drag and gravitational forces. The size range is from about 0.2 µm (or 0.5 µm) to about 10 µm. The minimum size measured depends on the instrument design. This method can provide high-resolution aerodynamic size distributions in real time (McMurry, 1998).

Electric mobility analyzers classify particles according to electrical mobility, which depends on the number of elementary charges carried by the particle, the magnitude of the elementary unit of charge, a slip correction factor, the absolute gas viscosity, and the particle diameter, but does not depend on particle density. Currently, the differential mobility particle sizer (DMPS; Keady et al., 1983) is used to determine size distributions based on electrical mobility. DMPS includes a differential mobility

analyzer (DMA; Liu and Pui, 1974b; Knutson and Whitby, 1975) and a particle detector, typically a CNC.

In the DMA, particles receive a bipolar charge. Particles in a narrow mobility range are determined by the classifying voltage and flow rates. The complete size distribution is obtained by carrying out measurements at a number of classifying voltages. Size distributions typically require about 20 minutes to obtain; although shorter time frames are obtained by ramping the classifying voltage continuously. The voltage scanning approach is now typically used in determining atmospheric aerosol size distributions. Diffusion limits the lower size of particles that can be accurately measured using the DMPS to particles greater than 0.05 - 0.1 \mu m; although recent work, summarized in McMurry (1998) describes approaches for determining particle sizes down to 0.003 µm. Sizing particles at the high end of the size spectrum is limited to a maximum size of about 1 \mum. This limitation results because particles larger than about 1 μm in diameter contain a wide range of charges, and, therefore, apparent sizes. Multiple charges increase the difficulty of deconvoluting the data to determine the contribution of each size at a given classifying voltage. Measurement accuracies are affected by particle shape and are likely size dependent, but can not be determined at this time due to the lack of polydisperse aerosol standards (McMurry, 1998).

Diffusion of particles to a surface is a function of particle size with diffusivities increasing with decreasing particle size. Diffusion batteries are based on this size-dependent deposition rate. They are most commonly used for particles less than 0.1 µm in diameter, as diffusion coefficients are sufficiently high enough to result in significant deposition across the collection surface. The lower limit is around a few nm in diameter. The quality of data that can be obtained with diffusion batteries is limited due to the stochastic processes that govern diffusion. Thus, a wide range of particle sizes is deposited on each collecting surface, with the result that there is no simple relationship between the change in aerosol concentration collected across the collecting surface and particle size. Therefore, in recent years diffusional separation has been replaced by electrostatic classification as described above.

### **A.2.5** Water Associated With Particles

The measurement of water associated with particles is problematic, as it must be done without disturbing the particle/gas-phase water equilibrium. Several methods have been used, including microwave resonance (Ho et al., 1974), gravimetric analysis at varying relative humidities (Hänel and Lehmann, 1981), beta-gauge measurements of mass at varying relative humidities (Speer et al., 1997), and measuring particle mobility at two different relative humidities using the tandem differential mobility analyzer (TDMA) (Rader and McMurry, 1986; Saxena et al., 1995; McMurry, 1998). The TDMA measures water associated with particles in the  $0.02 - 0.5 \,\mu m$  size range; although work is underway to expand this range to particles of 1 \mu m in diameter by using an aerosol concentrator (McMurry, University of Minnesota, personal communication, 1998). Other possible but less accurate methods for estimating water associated with particles involves measuring the difference in scattering properties of particles at two temperatures using two nephelometers, one at ambient temperature and one heated (Richards, STI, personal communication, 1998), and measuring the difference in mass on two TEOMs at two different sampling temperatures. The advantage of these last two methods, if they can be shown to provide suitable estimates of water associated with particles, is that they are much less expensive and are easy to use.

None of these methods provides direct measurements of water content as all methods involve taking the difference between two parameters (e.g., mass, scattering, mobility) and do not detect hydrated water; rather they detect condensed water that is in equilibrium with the gas-phase, based on varying relative humidity or varying temperature. An independent method relies on the use of thermodynamic models to calculate water content (e.g., Pilinis et al., 1989). However, these models only include water associated with ionic species (e.g., sulfate, nitrate, and chloride) and do not include water associated with organic material, which has been shown to be important (Saxena et al., 1995; Saxena and Hildemann, 1996). Since water can contribute significantly to aerosol mass, (e.g., 50% of the fine particle mass at relative humidities exceeding 70%; Hänel, 1976; Zhang et al., 1993), it is important that methods to measure water associated with particles be developed.

# A.3 Measurements in fogs and clouds

Fog and cloud collectors are designed to collect water droplets in the size range from 2 to 50 µm, as opposed to the collection of atmospheric particles that typically are sampled in the less than 10 µm or less than 2.5 µm size ranges. Collectors that collect all droplet size ranges are referred to as bulk collectors, while others collect two or more independent size fractions. Fog and cloud droplet collectors, typically collect the water droplets by impaction on a surface, either actively or passively. If the collection surface is moving or if air and droplets are being drawn across the collection surface, then the sampler is referred to as an active sampler. Passive samplers rely on air movement due to atmospheric flow to move the droplets across the collection surface. Pandis et al. (1995) recently reviewed fog and cloud droplet samplers. Table A-7 presents a summary of measurement techniques for fog chemistry.

## A.3.1 Bulk fog/cloud water detectors

These fog samplers collect all drop sizes in a single fraction. Passive samplers consist of a collection surface and a plate or a series of strings or rods. Fog impacts the collection surface and is collected by gravity in a container for additional analysis in the laboratory. The design of the collection surface and the speed of the wind define the size range of droplets collected. These collectors are used in areas where power is difficult to obtain.

Active samplers developed since the early 1980s are summarized in Pandis et al. (1995), while ones developed prior to the early 1980s are summarized in Jacob et al. (1984). The most recent methods for collecting fog droplets use a fan to pull air across Teflon stands (Demoz et al., 1996). Teflon strands are used in the Caltech Active Strand Cloudwater Collector (CASCC; Daube et al., 1987; Demoz et al., 1996) and in a later version of the CASCC (CASCC2; Collett et al., 1994; Demoz et al. 1996; Rao and Collett, 1995). The CASCC series of fog collectors have been widely used in fog experiments in the United States (see Pandis et al., 1995). The CASCC and the CASCC2

Table A-7. Measurement of Fog Chemistry

Method	Variable	Limit of Detection (µN)	Precision <sup>1</sup> (relative standard deviation %)	Accuracy	Comments	References
pH electrode	H <sup>+</sup> (as pH from 2.9 – 7)		(0.05 pH units)			Collett et al. (1994)
Ion Chromato-graphy	Cl	1.4	5.1	8%		Collett et al. (1997)
	NO <sub>3</sub>	0.8	0.3	7%		Collett et al. (1997)
	SO <sub>4</sub>	1.3	1.1	Better than 5%		Collett et al. (1997)
	Na <sup>+</sup>	0.9	1.2	Better than 5%		Collett et al. (1997)
	NH <sub>4</sub> <sup>+</sup>	1.2	0.6	Better than 5%		Collett et al. (1997)
	K <sup>+</sup>	1.0	3.1	Better than 5%		Collett et al. (1997)
	Mg <sup>+2</sup>	0.8	5.3	Better than 5%		Collett et al. (1997)
	Ca <sup>+2</sup>	0.9	4.2	Better than 5%		Collett et al. (1997)
	Acetate	1.1	2.6			Collett et al. (1997)
	Propionate	2.0	7.9			Collett et al. (1997)
	Formate	2.0	0.7			Collett et al. (1997)
	Pyruvate	0.8	0.2			Collett et al. (1997)
	Oxalate	5.45	0.7			Collett et al. (1997)
Colorimetric	S(IV)	0.9	14.4		Sample preserved in the field	Collett et al. (1997)
	HMS	0.9	14.4		Sample preserved in the field	Collett et al. (1997)

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Samples collected using a variety of fog collectors. Precision represents analytical uncertainty based on replicate measurements of the same sample. Overall uncertainty would be slight higher due to uncertainty in sampling flow rates. In percent unless noted otherwise.

Table A-7. Measurement of Fog Chemistry (continued)

Method	Variable	Limit of Detection (µN)	Precision <sup>1</sup> (relative standard deviation %)	Accuracy	Comments	References
Fluorescence	Formaldehyde	0.2	5.3		Sample preserved in the field	Collett et al. (1997)
Fluorescence	H <sub>2</sub> O <sub>2</sub> /Organic Peroxides	0.5	5.6		Sample preserved in the field	Collett et al. (1997)
Total organic carbon analyzer	TOC	1.3	10.8		OC converted to CO <sub>2</sub>	Collett et al. (1997)
	TDOC	1.3	10.8		OC converted to CO <sub>2</sub>	Collett et al. (1997)
Graphite Furnace Atomic Absorption	Iron	1.8	5.0		With Zeeman correction	Collett et al. (1997)
	Manganese	0.2	8.6		With Zeeman correction	Collett et al. (1997)

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both have 50% collection efficiencies or droplet size cutpoints at about 3.5 µm. The CASCC is a larger instrument operating at about 24.5 m³ min⁻¹, while the CASCC2 is considerably smaller and operates at 5.8 m³ min⁻¹. Fog or cloud droplets can be colleted with a time resolution of about 5 to 10 minutes using the CASCC and about 20-30 min using the CASCC2. Comparison of liquid water content obtained from the CASCC, CASCC2 and an independent technique, the Gerber Particle Volume Monitor showed good agreement (PVM-100) (Gerber, 1989; 1991). Fog or cloud water samples collected using these samplers can be analyzed for chemical species, as described below, and for liquid water content as described in Demoz et al. (1996).

#### A.3.2 Size-Selective Collectors

Several instruments have been designed to collect fog and cloud droplets in two or three size fractions (Noone et al., 1988; Munger et al., 1989; Schell and Georgii, 1989; Hindman et al., 1992; and Collett et al., 1993, 1995). These samplers either use multiple rows of strands in series, where each row consists of a different size strand, and therefore, collects different size droplets, or they consist of impaction plates similar to particle impactors with different size acceleration nozzles in each plate. As an example, the size fractionating CASSC (sf-CASSC) operates at 19 m<sup>3</sup> min<sup>-1</sup>, uses two rows of Teflon stands in series, and collects fog in two size ranges, greater than 23 µm and between 4 and 23 µm in diameter (Munger et al., 1989a; Demoz et al., 1996). As with the other strand collectors, drops impacting on the stands drain into collection vials below the sampler. This sampler, as with its bulk counterpart can collect tens to hundreds of ml per hour of liquid water (depending on the water content of the fog or cloud) and provides sufficient sample for chemical analysis of the collected fog or cloud water. However, the cutpoint efficiency is not as sharp as those described below that use impaction plates, similar to particle impactors. Other size-selective strand collectors are described in Pandis et al. (1995).

Collett et al. (1993) describe a two-stage cloud impactor that provides lower size-cuts (50 % collection efficiecy) of 3 and 10 µm diameter at a flow rate of 418 1 min<sup>-1</sup>. Thus, two size fractions are obtained, one above 10 µm and one between 3 and 10 µm in

diameter. Because the fog water sample is split into two fractions, sampling times on the order of 30-60 min are required to collect sufficient sample for chemical analysis. A three-stage impactor, larger than the two-stage impactor is described by Iovinelli (1994) and Collett et al. (1995). This collector operates at 1500 l min<sup>-1</sup>. The three-stage and a modified two-stage collector were designed with interchangeable impaction plates allowing for the collection of different size ranges with lower size cuts of 3, 5, 10, 14, and 21 µm droplet diameter for the two-stage collector and 3, 4, 10, 12, 15, 20, and 30 : m for the three-stage collector. Only two or three size ranges are collected, respectively, during a given sampling period (Pandis et al., 1995). Recently a five-stage cloud impactor has been developed (Collett et al., 1998) which simultaneously collects droplets with lower size cuts of 4, 10, 15, 25, and 30 µm droplet diameter. This latter sampler has been designed, not only to collect additional simultaneous size fractions, but operates at a higher volume (2,000 l min<sup>-1</sup> versus about 500 l min<sup>-1</sup>) is more compact, and uses a single rectangular acceleration jet rather than a series of circular jets. The smaller size of the collection area also helps to minimize contamination.

# A.3.3 Liquid water content of fogs and clouds

Several intercomparisons for estimating liquid water content by various methods have been conducted (Arends et al., 1992; Berner, 1988; Baumgardner, 1983; Demoz et al., 1995). Methods included in the various comparisons, although not all at the same time, were the Gerber Particle Volume Monitor, the Forward Scattering Spectrometer Probe (FSSP-100); and estimates from fog collectors. A summary of these intercomparisons is given in Pandis et al. (1995). The Gerber Particle Volume Monitor estimates liquid water content by measuring light scattered in the near forward direction by fog or cloud droplets passing between a laser source and a detector (PVM-100; Gerber 1989; 1991). This instrument is becoming popular for measuring liquid water content in fogs and clouds. Estimates of liquid water content from fog collectors are also becoming more popular, but they are complicated due to the need to correct for the collection efficiencies for each collected size fraction. Demoz et al. (1996) describe the calculations and uncertainties for the active strand series of cloud/fog water collectors. Agreement

among the different methods observed during these intercomparisons for the estimation of liquid water content in fogs and clouds was typically within 10%, with the exception of the FSSP-100 and the PVM-100, where the FSSP-100 estimated values 20-30% higher than the PVM-100 (Arends et al., 1992). Using gravimetric filter sampling as the reference for the study, Arend et al. (1992) determined that the best performance was obtained with the PVM-100.

### A.3.4 Chemical composition of fog and cloud droplets

Several inorganic and organic anions and cations are typically determined in fogs to elucidate the chemical behavior and dynamics within fogs and clouds (see for example, Collett et al., 1997; Collett et al., 1998a; Collett et al., 1998b; Jacob et al., 1989; Munger et al., 1983; Collett et al., 1989). Important species analyzed include inorganic anions (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>=</sup>), inorganic cations (H<sup>+</sup> [as pH], Na<sup>+</sup>, K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup>), total Fe and Mn, low molecular weight organic anions (formate, acetate, propionate and pyruvate and others), formaldehyde, S(IV), hydroxymethylsulfonic acid (HMSA), hydrogen peroxide, and organic peroxides. Successful determination of some of these species requires stabilization in the field immediately after sample collection. In general, the analytical methods for determining the concentration of these species in fogs and clouds are now well established and will only be summarized here. Analytical limits of detection and analytical uncertainties are given in Collett et al. (1997) based on results from the 1995 Integrated Monitoring Study (IMS95; Solomon et al., 1996). The reader is referred to Pandis et al. (1995) and Collett et al. (1997) for additional details.

In the methods described below, sample concentrations are determined against calibration curves of response against known concentrations, with corrections for blanks and interferences where known. Ambient concentrations are determined by knowing the total volume of water collected and air volume sampled. Precision is typically determined by analysis of split samples; although in a few cases it was determined by analysis of replicate standards. Examples of quality control, quality assurance, and data validation procedures are summarized in Collet et al. (1997). Detailed descriptions of how uncertainties and detection limits can be calculated for fog sampling is also given in

Collett et al. (1997) along with calculated values determined based on the experience with IMS95, and intercomparison results.

## <u>рН</u>

Collected fog or cloud water pH is determined immediately after sample collection with a combination electrode pH meter. The hydrogen ion concentration can then be determined from pH by standard methods. Precision has been determined for pH measurements in fog samples by making 10 replicate pH measurements each from separate aliquots of 18 different fog and cloud samples with pH values ranging from 2.9 – 7.0. Standard deviations from the 10 replicate measurements ranged from 0.01 to 0.11 pH units. The standard deviation tended to increase as sample pH increased. Only two of the eighteen samples had standard deviations greater than 0.05 pH units. Both had mean pH values greater than 6.2 (Collett et al., 1994).

# Inorganic anions and cations (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>-</sup>, Na<sup>+</sup>, K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>+2</sup>)

These species are most often determined by ion chromatography. Example analysis conditions are given by Collett et al. (1997). Metal cations can also be determined by atomic absorption spectroscopy and ammonium ion  $(NH_4^+)$  by automated colorimetric analysis. Limits of detection by these methods are similar.

### Organic acids

These species are most often determined by ion chromatography. Example analysis conditions are given by Collett et al. (1997).

# Total S(IV) and hydroxymethanesulfonic acid (HMSA)

Free S(IV) in cloud or fog water can be easily oxidized by dissolved oxidants  $(H_2O_2, O_3, \text{ and } O_2)$  in the presence of transition metals. Therefore, samples are preserved

immediately after collection by adding a preserving solution containing formaldehyde, sodium hydroxide, and CDTA (trans-1,2-cyclohexylenedinitrilo-tetraacetic acid). Addition of the preserving solution allows free S(IV) to be complexed with formaldehyde to form hydroxymethane sulfonic acid (HMSA), which is not easily oxidized. The HMSA is decomposed to free S(IV) before analysis. The CDTA is added to prevent interferences form trace metal and a catalyase solution is added to destroy any  $H_2O_2$  in the collected sample, since oxidation of S(IV) by  $H_2O_2$  is fast and could interfere with the measurement.

HMSA originally present in the fog or cloudwater sample is preserved as described above for S(IV), however, excess  $H_2O_2$  is first added to remove free S(IV) present in the sample. Free S(IV) is then determined by difference.

The analysis of S(IV) complexed as HMSA plus HMSA, and HMSA by itself is performed as follows. First, HMSA is decomposed to formaldehyde and S(IV) by a strong base followed by reaction of S(IV) and formaldehyde with acidic pararosaniline to form a purple compound that is measured spectroscopically.

# Formaldehyde (CH<sub>2</sub>O)

Formaldehyde needs to be preserved in the fog or cloudwater samples immediately after collection. This is done by adding bisulfite to form HMSA. In the laboratory, HMSA is decomposed to formaldehyde for analysis by fluorescence. Formaldehyde reacts quantitatively with 2,4-pentanedione and ammonia to from a yellow product, diacetyldihydrolutidine (DDL). The concentration of DDL is then determined by fluorescence spectroscopy.

## **Hydroperoxides**

Hydrogen peroxide and soluble organic hydroperoxides need to be preserved immediately after sample collection. This is done by adding p-hydroxyphenylacetic acid (POPHA) and peroxidase to form a stable dimer, and a conditioning reagent. The conditioning reagent contains potassium hydrogen phthalate (KHP), which acts as a

buffer (pH = 5.5), and EDTA that prevents interference by metal ions and also acts a buffer in the same pH range. The hydroperoxides are then determined as the dimer by fluorescence spectroscopy, since there is a 1:1 correspondence between the dimer and hydroperoxides.

### Total Fe and Mn

To stabilize these species in the field, fog and cloud samples are acidified with nitric acid immediately after collection. Concentrations are determined by either atomic absorption spectroscopy or graphite furnace atomic absorption spectroscopy (GFAAS). Collett et al. (1997) employ Zeeman corrected GFAAS.

# Total organic carbon (TOC) and dissolved organic carbon (DOC)

In the field after sample collection, fog or cloudwater is split into two fractions. The first fraction is added directly to a clean glass vial that provides a sample for the determination of total carbon and total inorganic carbon. The difference represents an estimate of total organic carbon. The second fraction is filtered before adding it to a second clean glass vial. This sample is analyzed for dissolved carbon and dissolved inorganic carbon with the difference representing an estimate of dissolved organic carbon. The collected samples are analyzed using a total organic carbon analyzer. Total carbon content is obtained by vaporization and decomposition of the sample at 680 °C, with measurement of evolved CO<sub>2</sub>. Inorganic carbon is determined by reacting the sample with 25% phosphoric acid followed by the measurement of evolved CO<sub>2</sub>. Elemental carbon is not measured by this method since the furnace temperature is too low to oxidize it to CO<sub>2</sub>.

## A.4 Meteorological measurements

## A.4.1 Temperature

Accurate measurements of temperature at ground-level and aloft are essential for understanding the kinetics of atmospheric processess and for determining boundary layer characteristics (e.g., the height of the boundary layer and its structure). Ground-level methods are routine, precise, accurate, and inexpensive. Measurements aloft are somewhat more expensive and typically less accurate since calibration methods are difficult. Table A-8 presents a summary of measurement methods for atmospheric temperature.

## Measurements at the Surface

Most *in situ* temperature measurements use the fact that many electrical properties are a known function of temperature. Instruments are based on resistance variation (thermistors), capacitance or thermocouple. The time constant for adjustment to a new temperature is a few seconds and the accuracy is better than 1°C. The sensor must be placed in a ventilated housing to shield it from direct solar radiation. The best instruments are ventilated by a fan, rather than relying on the wind.

### Measurements Aloft

The instruments used to measure temperature at the surface can be installed on an airborne platform (e.g., aircraft or radiosonde) to obtain data aloft. For measurements conducted with a radiosonde (see Section A.4.3 for a brief description of the tracking system), the vertical resolution of the measurement is in the range of 5 to 10 m. The signal typically can be tracked up to about five kilometers of altitude, depending on the meteorological conditions. However, the temperature data obtained by radiosondes vary in both space and time as the balloons are carried by the wind, and the amount of information is rapidly limited by the costs associated with the instrument platform.

Table A-8. Measurements of temperature

Method	Variable Measured	Range	Resolution	Accuracy	Potential Interferences/ Artifacts	Comments	References
Thermistor	Temperature	-40 to + 70°C	0.1°C	0.1°C (>0°C) 0.2°C (<0°C)		Needs ventilated housing	Sutron
Platinum resistance	Temperature	-30 to +70°C	0.1°C	0.3°C			Handar
Capacitive bead	Temperature	-90 to + 60°C	0.1°C	0.2°C	Accuracy degrades at high altitude	Radiosondes, upper air	Vaisala
Satellite sounding	Temperature profiles	Complete range of possible temperatures		~1°K	Influence of first guess	Low vertical resolution. Global coverage	J. Clim. Appl. Meteor., 24, 128-143, 1985
RASS	Virtual temperature	Normal range of temperatures		0.5°K	Accuracy varies according to meteorological conditions	Measured volume: a few hundred meters	Remtech

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Remote sensing techniques can be used to measure temperature aloft; then, the temperature data are recorded continuously as a function of height above a fixed ground location.

Since everything emits infrared radiation which depends on temperature, one can in principle measure temperature remotely by measuring the emitted radiation. That is the principle of satellite temperature profiler. The radiation emitted by the carbon dioxide of the atmosphere is measured at several wavelengths that have different emissivity and absorptivity. Since the carbon dioxide mixing ratio is approximately constant, the emission depends mainly on temperature. Simply stated, one can say that the radiation received by the satellite at each wavelength has been emitted by a different layer of the atmosphere. If the absorptivity at that wavelength is high, the emitting layer is at high altitude since radiation emitted by the lower layers is absorbed before reaching the satellite. Conversely, low absorptivity wavelengths come mainly from the lower layer where the density and temperature are high.

The early methods to convert the radiation measurements to temperature profiles were based on statistical regression. They were fast and robust, but not very accurate. Current methods make use of the radiative transfer equation. As mentioned above, these methods require the use of a first guess of the temperature profile, which introduces some uncertainty in the estimation of accuracy.

Another remote sensing technique is the ground based radio-acoustic sounding system (RASS). It operates in conjunction with a radar wind profiler. Pulses of microwaves and acoustic waves are sent vertically. Virtual temperatures are recovered by measuring the electromagnetic energy scattered from the acoustic wavefront (Virtual temperature is the temperature that dry air would have if it had the same density as the actual moist air at the same pressure. The RASS actually measures the air density and the temperature is derived from the perfect gas law. However, since the humidity is not known, one uses the gas constant for dry air and one obtains the virtual temperature). The propagation speed of the acoustic wave is proportional to the square root of the virtual temperature. Coincident measurements of humidity are needed to recover temperature. The vertical resolution obtained with a RASS is typically of the order of 50 - 100 m. The

maximum vertical range is typically of the order of a couple of kilometers, and the lowest level of measurement is typically centered at about 100m.

### A.4.2 Humidity

Measurements of humidity are essential for understanding the chemical characteristics and chemical equilibrium between the gas and particulate phases of atmospheric aerosols. Ground-level measurements are routine, accurate, and inexpensive, except at high relative humidities above about 95 – 98% depending on the sensor. Measurements aloft are somewhat more expensive and typically less accurate since calibration methods are difficult. Table A-9 presents a summary of methods available to measure relative humidity.

## Measurements at the Surface

There are many methods of measuring humidity. One is to measure the change of capacitance of a thin film with moisture. Other sensors use the change in electrical resistance of a thin film with humidity.

Wet and dry bulb sensors measure the differential temperatures of two standard electronic temperature sensors in ambient conditions. One sensor has its probe covered by a wick which remains in a moistened condition by absorbing water from a reservoir. This "wet bulb" sensor has a lower temperature reading owing to the cooling effect of evaporation of moisture from the wick. One can then calculate the ambient relative humidity by comparison between the dry and wet bulb temperatures.

Dewpoint sensors are based on the fact that moisture condenses as dew on a cooled surface. Typically, a chilled mirror is used. Condensation on the mirror drastically changes its reflectivity, thus making it possible to measure the dewpoint accurately.

Table A-9. Measurements of humidity

Method	Variable Measured	Range	Resolution	Accuracy	Potential Interferences/ Artifacts	Comments	References
Wet & dry bulb thermometers	RH computed from wet bulb temperature	0 to 100% RH		2% RH			Monitor Sensors
Chilled mirror	Dewpoint	-50 to + 100°C		0.2°C	Mirror could become contaminated with dust	Accuracy translates to about 5% in RH. More accurate at low humidity	EdgeTech
Thin film capacitor	Relative humidity	0 to 100% RH	1% RH	2 to 5% RH	About 1s lag. Possible wetting in clouds	Radiosondes, upper air	Vaisala
Raman lidar	Mixing ratio			.05 g/kg (night) 1 g/kg (day)	Background radiation interference during the day		Appl. Optics, 31, 3068-3082, 1992.

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#### Measurements Aloft

As for temperature, the measurement techniques used to obtain an estimate of relative humidity near the surface, can be installed on an airborne platform (e.g., aircraft or radiosonde) to obtain information on relative humidity aloft. For example, cooled mirrors are used in some airplanes. Typically, instruments based on a thin film capacitor or a carbon hygristor are used in radiosondes, because such instruments can be made very light. The spatial resolution and vertical range for relative humidity measurements are the same as for temperature. However, the same limitations as those mentioned for temperature apply; i.e., the measurements are limited in space/time and the cost rapidly becomes prohibitive. There are several remote sensing techniques that can be used to measure relative humidity as a function of height above a fixed ground location.

A promising experimental method of measuring moisture in the vertical direction is the Raman lidar developed by Sandia National Laboratories (NOAA in Boulder, CO). The Raman effect principle is that water vapor molecules that are excited by a beam of light at a certain frequency re-emit radiation at a different frequency. The return signal is proportional to the water vapor concentration. Comparisons with radiosondes during the Atmospheric Radiation Measurement program of DOE indicate that these measurements have high accuracy.

#### **A.4.3** Wind Speed and Direction

Measurements of wind speed and wind direction (WS/WD) are critical to understanding transport and mixing of pollutants within and above the boundary layer. Measurements at the surface are routine, precise, accurate, and inexpensive. Measurements aloft that are accurate are now obtained fairly routinely on a continuous basis. Compared to intermittent methods, they are not necessarily more expensive, given the wealth of added information obtained. Table A-10 summarizes measurement methods to characterize wind speed and direction.

Table A-10. Measurements of wind

Method	Variable Measured	Range	Resolution	Accuracy	Potential Interferences/Arti facts	Comments	References
Cup anemometer	Wind speed	0.5 to 50 m/s	0.1 m/s	2.5%	Can be affected by icing	Several models available with slightly different specifications	Monitor Sensors
Wind vane	Wind direction	0 to 360 deg	3 deg	5 deg	Can be affected by icing	Wind speed needs to be >0.2 m/s	Monitor Sensors
Ultrasonic	Wind components	0 to 65 m/s	Speed: 0.05 m/s Direction: 1deg	0.135 m/s 2 deg			Handar
Rawinsonde	Wind speed, direction	No limit	0.5 m/s 10 deg	.5 m/s 10 deg	Accuracy degreases at high altitude	Direction is truncated to tens of deg in the reports	Vaisala
Wind profiler	Wind components			0.75 m/s	Possible ground clutter	Profiles from 100m to 5000m in 50 – 100 m increments	J. Atmos. and Oceanic Tech. 12, 421-426, 1995
Doppler sodar	Wind components	0 to 45 m/s		0.25 m/s 2 deg		50 – 1500 m; 30 – 50 m for minisodars	AeroVironment
Doppler radar	Radial wind velocity	0 to 80 m/s		~2 m/s	Possible ground clutter. Aliasing of wind speed greater than range maximum	Signal strength depends on aerosol amount	Doviak and Zrnic, 1984

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#### Measurements at the Surface

The traditional method of measuring wind at the surface is with a three-cup anemometer, combined with a wind vane. The speed of rotation of the anemometer is proportional to the wind speed. Because of inertia, the anemometer cannot measure near calm winds (< 0.5 m/s) reliably, although lower wind speed thresholds, down to about 0.2 m/s can be obtained with precision and well maintained standard anemometers. Without special precautions, cup anemometers may also be sensitive to icing.

Hot wire anemometers detect the wind speed through minute temperature differences between wires placed in the wind and in the wind shade (the lee side).

Another method uses ultrasound to determine horizontal wind speed and direction (sonic anemometer). The measurement principle is based on transit time, the time it takes for the ultrasound to travel from one transducer to another, depending on the wind speed along the ultrasonic path. The transit time is measured in both directions. For zero wind speeds, the forward and reverse transit times are equal. With wind along the sound path, the upwind transit time increases and the down wind transit time decreases. Using these two transit time measurements, the instrument computes the wind speed along the path. The accuracy of the computed wind speed is independent of altitude, temperature and humidity. The method described for one path is repeated to determine the wind speed along each of three paths that are offset by 120 degrees with respect to each other. The micro-controller computes the wind speed and direction, as well as the rectangular components.

For calm conditions with wind speeds less than 1 m/s, and certainly less than 0.5 m/s, the use of sonic anemometers is recommended since these instruments can detect wind speeds as low as 0.05 m/s whereas standard cup anemometers typically have higher thresholds as mentioned above.

## Measurements Aloft

In the free atmosphere, the traditional way of measuring the wind is by following a radiosonde as it ascents (also called rawinsonde or pilot balloon). A radio theodolite

measures the azimuth and elevation angles of the balloon relative to the ground station as the balloon rises. The tracking is done automatically using the radiosonde transmitter signal (some systems use optical tracking, which is not as reliable as radio tracking). Upper air winds are then calculated by the computer from the theodolite data. The spatial resolution for wind measurements is typically of the order of 50 m (i.e., coarser than for temperature and relative humidity measurements) with a vertical range of several kilometers (typically 3 to 5 km, but possibly up to 10 km). However, these measurements provide data at specific times only, and temporal resolution is limited by the number of rawinsondes released.

For continuous measurements, several techniques exist. For example, radar wind profilers are now used in many field measurement programs. A wind profiler operates by transmitting electromagnetic energy into the atmosphere and measuring the strength and frequency of backscattered energy. The Doppler shift of the returned signal gives a measure of the air motion. By making measurements in several directions and averaging over a few minutes to eliminate the effect of turbulence, the total wind vector can be measured. The vertical range of a radar profiler is typically of the order of 5 km with a resolution of about 50-100 m.

The wind profile can also be measured with a Doppler sodar, which is based on the same principle as the radar wind profiler, but uses sound waves instead of electromagnetic waves. The altitude range sampled by a sodar varies according to the frequency used in the instrument, but also according to the environmental conditions (e.g., atmospheric turbulence, background noise). A "mini-sodar" with a frequency of about 4 KHz will typically have a vertical range from about 15 m to a few hundred meters. A "mega-sodar" with a frequency of less than 1 KHz can have a range of up to a few kilometers. The spatial resolution varies from about 10 m for a mini-sodar to about 100 m for a mega-sodar. Comparison of sodar measurements with tower-based measurements showed good agreement with a correlation of 0.92 (Crescenti, 1997).

Doppler radars work on the same principle as wind profilers, but instead of a fixed, phased array antenna pointing vertically, the antenna is a rotating dish. The wind speed in the direction of the beam can be mapped over several hundred km<sup>2</sup>. By processing the signal, the complete horizontal wind field can be retrieved. Doppler

radars can only measure radial winds within a certain range (the Nyquist interval); if the actual winds are outside that range, they will be aliased, that is they will appear to "wraparound" to the opposite value. The reason for this aliasing is the fact that the radar pulse has a finite length. When a Fourier transform is applied to the return signal to get its frequency spectrum, only a limited band of frequencies can be obtained. Any frequency shift larger than a certain limit (corresponding to strong wind) will be aliased to a different value of the opposite sign. By using special processing of the results, which assumes continuity of the wind speed, some of this aliasing can be eliminated.

## A.4.4 Mixing Height

The mixing height can be deduced from vertical temperature profiles. In addition, some sodars and radar profilers can provide information on the mixing height (Lindsey et al., 1996). These instruments use the fact that the radar reflectivity is related to the refractive index structure parameter and that this parameter peaks at the top of the convective mixing layer (i.e., bottom of the inversion layer). Typically, low level inversions (e.g., less than 300 m above ground level) cannot be resolved using this technique.

#### A.4.5 Solar Radiation

Pyranometers and radiometers that measure the solar radiation are based on the photo-voltaic principle. Various shading geometries make it possible to measure the direct solar radiation or the indirect radiation scattered by the whole sky. Some instruments measure total solar radiation whereas others measure U.V. radiation. Table A-11 summarizes the typical characteristics of photo-voltaic instruments.

### A.4.6 Fog and Clouds

A discussion of techniques to measure the liquid water content of fog was provided in Section 3.4. The spatial coverage of fog can be determined via human

Table A-11. Measurements of solar radiation

Method	Variable Measured	Range	Resol ution	Accuracy	Potential Interferences/ Artifacts	References
Pyranometer (silicon photovoltaic)	Total solar radiation	Whole range of daylight conditions	2 Wm <sup>-2</sup>	3 to 5%	Slight temperature dependence	Sutron

observations, measurements or satellite data. First, an operational definition of fog is needed to characterize the spatial extent of the fog. Standard procedures from the National Weather Service define fog to be present when atmospheric visibility (visual range) is 6 miles or less and relative humidity is 86% or more (dew point depression of 4°F or less). Visibility less than 6 miles with relative humidity less than 86% is defined as haze. These definitions are arbitrary and are, therefore, subject to uncertainties. Automatic visibility sensors can be used in conjuction with measurements of relative humidity to record the presence of fog. Satellite data that provide enhanced fog imagery may be very useful for areas where the areal coverage of the fog is significant.

The presence of clouds can be determined via human observations, airborne measurements, and satellite data. Trained human observers will report estimated height and type of clouds, following National Weather Service procedures. However, human observations are generally limited in their spatial coverage. Aircraft have been used to sample in clouds and can, therefore, characterize the liquid water content. Satellite imagery is particularly useful to characterize cloud coverage over large regional domains.

Ceilometers are lidars that measure the height of clouds. For example, Vaisala makes one that can detect 3 cloud layers simultaneously, up to 7.5 km in height. Vertical resolution is 50 ft with an accuracy of 25 ft. It uses special transmitting and receiving optics so that beam overlap is almost eliminated and detection of thin clouds as low as about 15-50 m above the ceilometer is possible.

#### A.5 Emission Inventories

An emission inventory plays a vital role in various aspects of current air quality management practices. Emission inventories are used to assess contributions of individual sources or group of sources in a region, as input data for source-oriented air quality models, and in the development and implementation of control strategies. The requirements (in terms of their spatial and temporal resolution) for emission inventories in modeling applications are significantly more demanding than for assessment studies. For example, emission inventories used for PM and visibility modeling need to be spatially and temporally resolved in a manner that is consistent with the model

formulation. Emission data for PM and visibility modeling need to be chemically resolved too, in order to adequately track the complex chemistry that occurs throughout a region of interest. A discussion of emission inventories can be based either on the type of sources of emissions (e.g., stationary, mobile) or on the emitted chemicals (e.g., SO<sub>2</sub>, NO<sub>x</sub>, VOC). Our discussion of emission inventory development uses the latter approach (Section A.5.1) but our discussion of testing emission inventory with field measurements is more conducive to using the former approach. A standard approach to estimate emissions of a pollutant is to use the following mathematical relationship:

$$E = \sum_{i} EF_{i} \cdot O_{i} \cdot (1 - \mathbf{h}_{i})$$
 (A-1)

where EF = Emission factor for the production of the pollutant by source i, e.g., amount of  $SO_2$  emitted per ton of coal burned, amount of  $NO_x$  per vehicle mile traveled

O = Operating rate or activity level of source i, e.g., tons of coal combusted by power plants, the distance traveled by motor vehicles

 $\eta =$  Efficiency of the control device used by source i

Emission factors are given in compilations (e.g., AP-42) or are calculated by emissions models (e.g., PART5 for motor vehicles, BEIS for biogenic hydrocarbon emissions). Uncertainties in emission estimates are due to uncertainties in each of the three terms on the right hand side of Equation (A-1). A discussion of uncertainties in estimating emissions using an emission factor-based approach is provided in Pai et al. (1998b). Additional uncertainties can arise due to exclusion of sources and the inability of annual average emissions (typically calculated using Equation A-1) to capture the temporal variability, e.g., seasonal or weekday versus weekend.

In Section A.5.1, we discuss the current emission estimation techniques and their limitations in estimating emissions from major source categories of atmospheric PM and the chemical precursors of secondary PM. In Section A.5.2, we review measurement

techniques that can be used to validate emission inventories for PM and visibility modeling.

## A.5.1 Current estimation techniques and their limitations

### Particulate Matter (PM)

The dominant sources of primary PM in the United States include fugitive sources of dust from unpaved roads, paved roads, farming operations, construction activities and wind erosion. Emission rates for fugitive dust are difficult to measure or model. In the National Particulates Inventory (E.H. Pechan, 1997), emission estimates for most source categories within the fugitive dust category were derived using the particulate emission factor equations from the AP-42 database (EPA, 1995). These source categories include agricultural tilling, construction activities, paved road resuspension, unpaved roads, wind erosion and cattle feed lots. While the AP-42 emission factor approach may have some validity when annually averaged over the United States, they introduce significant uncertainties when used to estimate contributions to a single receptor on a single day (Moosmüller et al., 1998). PM-10 and PM-2.5 emissions are calculated from the TSP (total suspended particulates) emissions by applying a source category-specific (e.g., utility, paved road, wind erosion) particle size distribution factor. These factors are typically developed based on information contained in AP-42 and on engineering judgment. The chemical speciation of PM species is accomplished using source category-specific PM profiles (e.g., Shareef and Bravo, 1988) which consist of percent contribution of each chemical species within each size fraction of interest.

### Sulfur dioxide (SO<sub>2</sub>)

Almost all (97%) anthropogenic  $SO_2$  emissions are from stationary sources (defined as all sources of emissions except highway and off-highway vehicles and natural sources). As a portion of total stationary source emissions, point sources (defined as fairly large facilities) contribute 94% of  $SO_2$ , from which the electric utility power plants

are the largest source of SO<sub>2</sub> emissions, contributing 67% in the United States Inventory (Saeger et al., 1989). The non-utility sources in the inventory include industrial combustion, non-ferrous metal smelting, iron and steel industry, petroleum refineries, oil and natural gas production, pulp and paper, and cement manufacturing. Industrial combustion includes all industrial fuel use but combustion of bituminous coal results in most SO<sub>2</sub> emissions in this category. Non-ferrous metal smelting includes primary copper, primary and secondary lead, primary zinc, and primary aluminum smelting. SO<sub>2</sub> emissions in petroleum refineries result from processes such as catalytic cracking, flaring, process heaters, and sulfur recovery systems.

The activity rates for most  $SO_2$  sources are well known due to detailed production records that are maintained by individual facilities and submitted to local/state/federal regulatory agencies as part of permitting requirements. Emission factors characterizing the  $SO_2$  content in the fuel is also quite reliable. The uncertainty in  $SO_2$  emissions arises from the source-to-source variability that is not always captured in the emission factors that are universally applied to all sources within a source category.

# Nitrogen Oxides (NO<sub>x</sub>)

The anthropogenic NO<sub>x</sub> emissions in the United States inventory (Saeger et al., 1989) come from mobile sources (40-45%), power plants (30-35%), and other industrial sources (20%). About half of the NO<sub>x</sub> emissions associated with mobile sources come from the light-duty gasoline trucks and cars and approximately one-quarter are from heavy-duty gasoline and diesel vehicles. A significant fraction of NO<sub>x</sub> emissions includes biomass burning, lightning and soil emissions. In the United States, most of the NO<sub>x</sub> associated with biomass burning comes from wildfires. Lightning can be a significant source of nitric oxide (NO) due to the high temperature conversion of nitrogen (N<sub>2</sub>) and oxygen (O<sub>2</sub>) to nitric oxide (NO). NO<sub>x</sub> is produced in soils by the microbial processes of nitrification and denifrication and by several chemical reactions that involve nitrate. The variables that include NO<sub>x</sub> emissions from soils include soil temperature, moisture content, soil nutrient level, vegetation cover, fertilization and climate.

Like the anthropogenic sources of  $SO_2$  emissions, the emission estimates of  $NO_x$ from stationary sources are quite reliable in terms of the operating rate data and emission factors. The largest uncertainties in NO<sub>x</sub> emissions come from estimating NO<sub>x</sub> from mobile sources which account for nearly one-half of total NO<sub>x</sub> emissions in the U.S. inventory and more in some urban airsheds. Mobile emission estimates are generated by multiplying an estimate of vehicle activity by an emission factor specific to the process by which emissions are generated, e.g., tailpipe, evaporative, running loss (Maldonado, 1991). Vehicle activity data used to generate the emission estimates are typically generated by transportation planning models. However, the transportation planning models are primarily designed and used by transportation analysts to evaluate the effects of increased development on roadway level-of-service and to determine roadway capacity needs for local and regional planning (CARB, 1993). Most transportation models produce activity estimates only on an average daily basis and only for average weekday conditions. In reality, however, the levels of vehicle travel vary significantly by hour throughout the day and from week-days to week-ends as well. The inability of these models to resolve the temporal variation in mobile emissions could be a large source of uncertainty.

### Volatile Organic Compounds (VOC)

A large amount (40%) of the anthropogenic VOC emissions in the United States inventory (Saeger et al., 1989) comes from mobile sources. Solvent emissions resulting from evaporation of organic solvents and application of surface coatings are distributed across a broad group of sources and comprise 32% of total VOC emissions. Other sources such as industrial manufacturing activities and fuel combustion comprise the rest (28%). In the mobile source category, emissions from light-duty cars and trucks make up the largest contributing fraction. The mobile source hydrocarbon emissions result from incomplete combustion of fuel and lubricating oil in the exhaust and gases that leak from the engine, vaporization of fuel as a result of the heating of the fuel tank, vaporization of fuel from the heat of the engine after it has been turned off, vaporization of fuel from the fuel system while the vehicle is operating, fuel losses due to leaks and diffusion through

containment materials, and fuel vapor displacement as a result of filling fuel tanks. The vehicle activity data used to estimate mobile source emissions are uncertain as discussed above.

Organic solvent utilization accounts for the largest anthropogenic, non-mobile source of VOC emissions. These emissions result from the use of organic solvents in the dry cleaning industry, in metal degreasing, in cutback asphalt paving, and in a variety of consumer and commercial product manufacturing. The solvent emissions from surfacecoating-related industries include automotive furniture and appliance manufacturing, painting, and metal and plastic fabrication industries. The sources described above are generally numerous and small and, therefore, very cumbersome to track individually in an emission inventory. While the emissions from these sources are estimated individually, they are grouped together as area sources in an emission inventory. The typical cutoff to distinguish point and area sources in an emissions inventory is 10 tons/year based on annual emissions. Emissions from area sources are estimated either using the emission factor approach (Equation 3-1) or a material balance method. The material balance method is more appropriate for a solvent evaporation source. This method assumes that all solvent consumed by a facility (or in an area) is evaporated to the atmosphere and can be estimated using production or usage data. In addition to the uncertainties in emission factors discussed earlier, other sources of uncertainties in estimating emissions from area sources include exclusion of sources, double counting of emissions and lack of adequate spatial resolution due to lumping of various sources.

Each point and area source category of an emissions inventory is assigned a speciation profile (e.g., Shareef et al., 1988) that contains the weight percent breakdown of the individual species that make up the profile. These profiles are used to calculate the amount of each species from the total VOC emissions for each source category. Since the speciation requirement for VOC emissions may change depending on the chemical mechanism used in a particular application, it is desirable to keep speciation as flexible as possible. To achieve this flexibility the VOC emissions are speciated into a species list that is more comprehensive than the list of species needed for most chemical mechanisms available today (e.g., CBM4, RADM, SAPRC). For example the PSPLIT module of the NAPAP inventory divides the hydrocarbon emissions into 640 discrete species. This

comprehensive list is then reaggregated into classes based on the requirements of the selected chemical mechanism.

About 98% of the annual natural emissions of total VOC in North America are emitted from vegetation. Emissions from these sources are typically estimated using a numerical model known as the Biogenic Emission Inventory System (BEIS). The earlier versions of the model, BEIS version 1 (BEIS1) (Pierce and Waldruff, 1991) and BEIS version 2 (BEIS2) (Geron et al., 1994) were quite crude in their characterizations of biogenic emissions and chemical speciation. For example, BEIS1 used four categories to represent VOC: isoprene, α-pinene, other monoterpenes, and unidentified biogenic compounds. The current version of BEIS, BEIS3, provides emission estimates at a spatial resolution of 1 km<sup>2</sup>, for 35 individual VOC (isoprene, 2-methyl-3-buten-2-ol, 18 monoterpenes, 11 oxygenated VOC and 4 light hydrocarbons) and 3 lumped VOC categories. The BEIS model calculates emission estimates using an approach similar to Equation (A-1), with the individual terms representing the following: EF is the landscape average emission factor, O is the activity factor and  $(1-\eta)$  is the landscape escapes efficiency (i.e., the fraction of emitted biogenic compounds that escape the canopy). EF is calculated from estimates of plant species composition and species-dependent emission factors. The activity factor, O, accounts for the influence of environmental conditions, e.g., the effect of temperature on emissions. While the chemical speciation in biogenic emission inventories has significantly improved since the earlier versions of the BEIS model, the current speciation of BEIS3 places an emphasis on O<sub>3</sub> precursors, e.g., isoprene. The precursors of PM, especially those forming secondary organic aerosols are poorly represented in current biogenic emission models. For example, BEIS3 lumps other monoterpenes and sesquiterpenes into one "lumped VOC" category. This simplification can be a serious limitation in PM and visibility modeling.

### <u>NH</u><sub>3</sub>

Agricultural sources (i.e., livestock operations and fertilizer application) make up approximately 90% of ammonia emissions in the U.S. national inventory (E.H. Pechan, 1994). In regional emission inventories, other source categories also contribute a

reasonable amount, e.g., sewage treatment facilities in the San Joaquin Valley (SJV) inventory (STI, 1998). Currently, ammonia emissions for most source categories are calculated by multiplying emission factors and activity data. The emission factors are based on experimental data or best engineering judgement. Historically, the NH<sub>3</sub> emission factors for most source categories are obtained from the AP-42 (EPA, 1995) database. These emission factors are quite uncertain in some cases, and can vary over several orders of magnitude (e.g., fertilizer manufacture). The activity data for most sources of NH<sub>3</sub> emissions are typically obtained from survey responses. For example, in the U.S. inventory, the activity data for livestock NH<sub>3</sub> emissions were obtained from the 1992 Census of Agriculture (BOC, 1995). This data base has county-level estimates of number of heads for the following livestock: cattle and calves, hogs and pigs, poultry, sheep, horses, goats and minks. The activity data for fertilizer application were obtained from the Commercial Fertilizers Data Base (TVA, 1990). This data base includes county-level usage in 6-month increments of over 100 different types of fertilizers including those that emit NH<sub>3</sub>.

Due to the importance of NH<sub>3</sub> in the formation of secondary PM, a pilot-scale field study was conducted in the SJV to develop better emission factors for NH<sub>3</sub> from a dairy, a farm plot, and a wastewater treatment plant (Fitz et al.,1997). Such focused studies allow for a calculation of NH<sub>3</sub> emissions for cases where special circumstances may have influenced the activity of a given source, such as unusual meteorological patterns or variation in management practices. Similar studies have been performed in the Los Angeles area (Fraser and Cass, 1998).

# Overall inventory

Constructing an emission inventory for an Eulerian air quality model application can be viewed as involving two steps: (1) emission estimate calculation for each pollutant (i.e., PM, SO<sub>2</sub>, NO<sub>x</sub>, VOC, NH<sub>3</sub>) for individual sources (e.g., power plants) or source category (e.g., mobile sources) and (2) spatial, temporal and species allocation of the emission estimates in a manner consistent with the formulation of the air quality model. The calculation of emission estimates is based on Equation (3-1) and is a function of

three parameters: emission factor, activity rate and control device efficiency (or landscape escape factor). Few measurements of these three parameters are made at representative sources within each source category. These measurement data are then used to quantify the parameters which are then applied to all sources within a source category. In theory, a perfect inventory, within measurement uncertainties, can be generated by collecting continuous measurement data at all sources of emissions. However, it is not practical to do so, and, therefore, the overall quality of the emission estimates, is determined by how well the parameters represent all sources in a source category.

In the second step, surrogate variables are typically used to spatially, temporally and chemically resolve the emission estimates so that they are consistent with the requirements of the air quality model. Spatial allocation of point sources is quite accurately known from the plant-specific location data but the spatial allocation of area sources is usually accomplished using surrogate variables such as population or energy consumption, that might not properly characterize the variability of sources in a given source category. Similarly, temporal surrogate variables used to obtain hourly emission estimates might not reflect the real-world conditions (e.g., weekend versus weekday conditions for mobile sources). The chemical resolution of the emission estimates is typically governed by the chemical mechanism used in the air quality model.

#### A.5.2 Evaluation of Emission Inventories through Measurements

### Mobile emissions

Emissions of CO, VOC, NO<sub>x</sub>, and PM from mobile sources are an important source of air pollution in many urban airsheds. Tunnel studies using infared remote sensing (Stedman et al., 1994) provide an excellent means of validating emission estimates from mobile sources (Harley et al., 1997). Concentration of VOC, CO, NO<sub>x</sub> and PM can be measured at both the upwind and downwind portals of the tunnel and the emissions rate can be calculated based on their difference. Measured emission rates in tunnel studies in California (Pierson et al., 1990), eastern United States, (Robinson et al.,

1996) and Canada (Gertler et al., 1997) have been compared to predictions from emission factor models. The main advantage of tunnel studies is that they can be used to characterize emissions from a large random sample of on-road motor vehicles. The disadvantage is that tunnel measurements represent primarily mobile emissions from running losses and do not account for influence of cold start or evaporative emissions or the effect of high speed and heavy acceleration driving conditions. Furthermore, tunnel studies, as opposed to laboratory testing, cannot be used for controlled experiments to understand the effect of individual parameters, e.g., fuel composition, vehicle air conditioning.

Another area of improvement with respect to the mobile source emissions is to obtain better vehicle activity data than those provided by transportation models. The vehicle activity data should include temporal variability in travel activity (summertime versus wintertime, week-day versus week-end, peak morning hours versus afternoon hours), vehicle type distribution (automobile, light-, medium-, or heavy-duty truck) and type of road (freeway, arterial, collector or local). Such a high resolution of vehicle activity data was collected during the 1990 San Joaquin Valley field study (CARB, 1993). Vehicle counts were collected at several locations in the study region during the summer of 1990. These counts were made during mid-weekdays, as well as for Friday, Saturday and Sunday to develop day-of-the week correction factors. Hourly counts were also maintained during episodic days for the development of time-of-day distributions. Seasonal correction factors were developed by assembling count data for some days of the week during spring and fall months. To develop the vehicle type distributions, vehicle classification counts were kept each day of the week during the episode period for all hours of the day. The above database contained roughly 100 days of count data covering 220 locations. To supplement these data, classification counts were also made at several locations during the 1990 summer field study using either manual, mechanical and videotape techniques.

## **Stationary Sources**

Gaseous pollutants emitted from a significant number of large stationary sources in the United States are directly measured using continuous emissions monitoring systems (CEMS). Primary PM emissions are not measured on a routine basis. Data from the CEMS are generally superior to estimates made using emission factors or other estimation technique. This is to be expected since CEMS provides measurements of instack emissions levels, whereas emission factors were based on a small number of stack testing on plants that were not necessarily representative of the entire population of sources. Currently, all electric-utility power plants with nameplate capacity greater that 25 MW have installed CEMS that measures in-stack levels of SO<sub>2</sub>, NO<sub>x</sub>, CO<sub>2</sub> and stack gas volumetric flow rate. The CEMS usually consists of an emission analyzer, a diluent analyzer, and software for reporting and manipulating the measurements. The pollutant emission rates are estimated from CEMS measurements of pollutant concentrations (in ppm) and dilutant concentrations (%) using standard algorithms. Emission measurements from CEMS have had some system problems in some cases associated with calibration of flow meters, missing data substitution protocols, software errors and use of monitoring equipment outside the design range. However, these system-level problems are expected to decrease as the users gain more experience with the system.

#### Area Sources

Direct measurements of area source emissions such as CEMS for point sources, is not practical because (1) there are numerous individual sources and (2) activities associated with these sources are often hard to determine or are, at best, arbitrary. Techniques for estimating area source emissions from ambient data or remote sensing of emissions sources are in the experimental stages of development. Area source emissions are typically estimated using a top-down approach, i.e., allocating an operating rate that is known for a large area, such as a state or nation, to smaller areas and then applying an emission factor. A bottom-up approach, on the other hand, involves collection of locally available operating data through a comprehensive survey effort. While bottom-up

inventories are resource intensive, they are capable of providing better spatial and temporal resolution and are more appropriate for area source emissions. For example, a day-specific VOC and NO<sub>x</sub> emissions inventory was generated from numerous oil production sources in the San Joaquin Valley by gathering questionnaires containing daily operating data and collected by means of a postal survey (CARB, 1992).

Micrometeorological techniques can also be used to measure emission fluxes from biogenic area sources (Businger and Delaney, 1990). These techniques require the measurement of fluxes and gradients of one passive scalar such as heat, water vapor or carbon dioxide using fast response sensors. The measurements are then used to calculate a transfer coefficient K, which is assumed applicable to all passive scalars. The transfer coefficient and the concentration gradient can be used to calculate the above-canopy biogenic VOC fluxes. This technique has been used to calculate fluxes of chemically reactive species (Galmarini et al., 1997). The technique has limited use in areas with even moderately complex terrain.

Inverse modeling can also be used to estimate emissions from area sources. Inverse methods use existing air quality data and models of the transport and transformation processes to infer what the inputs would have to be in order to best fit model predictions to measured concentration. The techniques vary from simple approaches like source-receptor models (e.g., Cass and McRae, 1983) to more sophisticated Kalman Filter based approaches (e.g., Hartley and Prinn, 1993; Mulholland and Seinfeld, 1995).

### **Overall Inventory**

The overall emission inventory needs to be evaluated using independent data. The evaluation must address the absolute amount, relative composition, spatial pattern and temporal distribution of the emissions. Several methods have been used in the past for an overall inventory evaluation. These methods include both top-down and bottom-up approaches and include the following:

#### Reconciliation with ambient data

- Ground truth verification
- Modeling

Each of these methods is briefly discussed below.

#### Reconciliation with ambient data

Comparison of ambient data and emission inventories provides a quantitative evaluation of the relative composition of emissions. It is a form of top-down inventory evaluation. During the SCAQS-87 study comparisons of CO/NO<sub>x</sub> ratios and VOC/NO<sub>x</sub> ratios in the ambient air were made to evaluate the relative amounts of CO, VOC and NO<sub>x</sub> emissions in the SoCAB (STI, 1991). The SCAQS VOC data included a comprehensive set of individual C1-C12 hydrocarbon and C1-C7 carbonyl concentrations at several locations and aircraft measurements of VOC between 500 and 800 m above ground. This extensive set of speciated VOC data made it possible to compare the relative amounts of individual organic species and species groups measured in the ambient air with the VOC speciation of the inventory. The largest uncertainty in comparisons between ambient data and emission estimates is the fact the ambient measurements are influenced not only by fresh emission emitted near the source, but also by transport and chemistry. These uncertainties can be minimized by making the comparison during times when emission rates are high and the influence of other factors are low, e.g., low wind speeds and negligible chemistry.

# Ground truth verification

This method involves techniques that make direct comparisons between emissions estimates and some other known quantity that is related either directly to the emission source or indirectly to the underlying process that results in emissions (Mobley and Saeger, 1993). In contrast to the comparison against ambient data discussed above, this technique represents a bottom-up form of inventory evaluation. While this method can be resource intensive, it often provides a powerful method to evaluate the absolute form

of emissions. Ground truth verification techniques include detailed manual surveys of sources known to contribute significant emission magnitudes and monitoring studies at individual facilities. The use of CEMS would be an example of ground truth verification by monitoring at the stack.

### Modeling

Both source- and receptor-oriented models can be used to evaluate emission inventories. In receptor modeling, ambient data and the chemical composition profiles from selected sources are used to assess the contributions of different sources to the observed concentration of pollutants. The relative contributions of sources provided by receptor modeling can then be used to evaluate the emission inventories with some appropriate assumptions on transport and removal. Source-oriented three-dimensional models, on the other hand, attempt to treat all relevant atmospheric processes including emissions, transport, dispersion, chemistry and deposition. Assuming that we have included a comprehensive treatment of the relevant governing processes in the model and that the uncertainties in other model inputs (e.g., meteorology) are relatively small, it is reasonable to attribute deviations between model predictions and observations to uncertainties in the emission inventories. The model can also be used as a sensitivity tool to test known biases in the emission inventories; For example, Fujita et al. (1992) compared CO/NO<sub>x</sub> and VOC/NO<sub>x</sub> ratios in the emissions inventory and ambient concentrations in the Los Angeles basin. They concluded that the observed ratios were about 1.5 and 2-2.5 times greater, respectively, than the ratios in the emission inventory. Lu et al. (1997) used the SMOG modeling system to suggest that the emission inventory underestimated VOC emissions. Such approaches cannot be used as absolute tests of the emission inventories since there are many other sources of uncertainties in a model. Nevertheless, a large discrepancy between model predictions and observations may be pointed at the emission inventory, thereby suggesting the use of other techniques to better evaluate the emission inventory.

### A.6 Atmospheric Deposition

### A.6.1 Dry Deposition

Dry deposition refers to the transfer of airborne material, both gaseous and particulate, to the earth's surface, including soil, water, and vegetation, where it is removed. The dry deposition process consists of three distinct steps: (1) turbulent diffusion of the material through the surface layer to the immediate vicinity of the surface, (2) surface transport of the material through the laminar sublayer next to the surface to the absorbing component of the surface, and (3) removal of the material at the surface sites. Due to the complexity of the process, dry deposition is typically represented parametrically using the deposition velocity (v<sub>d</sub>), which is related to the flux of the material to the surface:

$$F_d = v_d c \tag{A-2}$$

where F<sub>d</sub> is the deposition flux, and c is the concentration in the bulk gas phase.

Collection of deposited material on a surrogate surface is generally considered not to be a very accurate method because deposition is a strong function of the surface type for most chemicals. Therefore, techniques that are based on micrometeorological measurements are recommended. Such techniques take advantage of the atmospheric mixing that integrates the different fluxes that occur over the various leaf and soil surfaces present in a particular canopy, thereby yielding values representative of the entire underlying surface. Two micrometeorological techniques that have been widely used to study the dry deposition of gases and particles are the gradient method and the eddy correlation method.

We discuss below these two methods and their application to gases and particles of interest in the PM formation, including ozone, NO, NO<sub>2</sub>, SO<sub>2</sub>, ammonia, PM-2.5, and PM-10. Chemical sensors suitable for these techniques are also briefly discussed.

#### Gradient Method

For a homogeneous and stable atmosphere, the vertical fluxes (F) of gases for a given layer can be determined as the product of the eddy diffusivity (K) and the concentration gradient measured:

$$F = -K \frac{\Delta c}{\Delta z} \tag{A-3}$$

where  $^{\Delta}c = c(z_2) - c(z_1)$  and  $^{\Delta}z = z_2 - z_1$ , the concentration and height differences at two sampling points. The determination of turbulent diffusivity presents a major difficulty for the application of this method. Horváth et al. (1998) used Monin-Obukhov's similarity theory and universal functions to determine K; however, such procedures can not be applied to complex surfaces such as forests. Alternatively, the Bowen Ratio Method (e.g., Lindberg et al., 1995) assumes that

$$F = F_s \frac{\Delta c}{\Delta q} \tag{A-4}$$

where  $^{\Delta\theta}$  is the difference in potential temperature at the two levels, and  $F_s$  is the vertical flux of latent heat. Lindberg et al. (1995) relaxed the assumption that the transport characteristics of heat and scalars are similar by using another scalar, such as  $CO_2$  or  $H_2O$  vapor concentration, as a reference. The flux of latent heat or chemical compound can be determined directly by eddy correlation measurements (see below).

Horváth et al. (1998) applied the gradient method to estimate the dry deposition velocities of NO, SO<sub>2</sub>, and O<sub>3</sub> above short vegetation (grass, wheat, and mustard plants) under both stable and unstable conditions. They determined the deposition velocity of O<sub>3</sub> and SO<sub>2</sub> to be 0.05-0.07 cm-s<sup>-1</sup> and 0.19-0.20 cm-s<sup>-1</sup>, respectively. NO emission was observed.

## **Eddy Correlation Method**

Eddy correlation is considered by many to be a relatively direct method for determining dry deposition. The basic idea is that the flux of a scalar can be determined as its covariance with the vertical component of wind, i.e.,

$$F = \overline{c'w'} = \overline{(c - \overline{c})(w - \overline{w})} \tag{A-5}$$

where the overbar denotes an averaged quantity and the prime denotes fluctuations around the mean value. In essence, the downward flux is large when downward fluctuations of wind are associated with high concentrations, and vice versa. The covariance represents the vertical component of the net flux at the height of the measurements; therefore, non-divergent and stationary atmospheric conditions are needed to infer the surface flux (see also Pederson et al., 1995).

Traditionally, eddy correlation measurements were made on fixed instrumentation towers. For example, diurnal profiles of deposition velocities for ozone were measured over three types of surfaces in the San Jaoquin Valley, CA (Massman et al., 1994). There is a large body of literature for deposition flux measurements of trace gases, such as SO<sub>2</sub>, NO, NO<sub>2</sub>, O<sub>3</sub>, CH<sub>4</sub>, etc. Gallagher et al. (1997) measured the deposition fluxes of submicron particles onto a forest surface using the eddy correlation method. Particle concentrations were measured with an optical counter. They found that the deposition velocities can be as large as 1 cm-s<sup>-1</sup> for particles in the size range of 0.3 to 0.5 µm.

Eddy correlation measurements can also be made from aircraft and other moving platforms. Although it is harder to meet the atmospheric conditions for valid inference of surface fluxes, aircraft measurements can effectively sample different surface types within the domain. Hubbe and Pederson (1994) claimed favorable comparisons between aircraft and ground based measurements of O<sub>3</sub> and CO<sub>2</sub> deposition fluxes in the San Jaoquin Valley, CA, over cotton, grape, and grass surfaces.

#### **Chemical Sensors**

The key requirement for determining dry deposition fluxes using the gradient method is obtaining accurate measurements of the concentrations of the chemical species of interest. Measurement sensitivity may be increased by increasing the averaging time of measurements, as long as the stationarity criterion of the atmosphere is satisfied. However, the requirements for accurate determination of fluxes using the eddy correlation method are more stringent. In addition to a fast response anemometer (e.g., a sonic anemometer with a frequency response of >10 Hz), chemical sensors with a frequency response of at least 0.5 Hz are also required. A 5 to 10 Hz response time is preferable for aircraft measurements. This excludes the application of the eddy correlation method to species such as HNO<sub>3</sub> and NH<sub>3</sub> for which fast response measurements are not easily available. Table A-12 compiles some chemical sensors that can be used to measure deposition fluxes of species relevant in the PM issue. Other chemical sensors, as described in Sections A.1 and A.2 may also be adapted for measuring fluxes (see also Pederson et al., 1993).

#### A.6.2 Wet Deposition

Wet deposition to surfaces and the ground is a significant removal process for atmospheric pollutants (Waldman and Hoffmann, 1987). Wet deposition includes precipitation in the form of rain and snow, fog, interceped clouds with mountains, and dew formation. The sections below briefly discuss deposition of atmospheric pollutants by these removal processes.

#### **Precipitation**

The amount of precipitation in the form of rain or snow has been monitored routinely for many years. These results are usually obtained by standard rain gauges or by measuring the depth of snow that has fallen on the ground. However, these methods do not provide samples that can be used for chemical analysis of the collected

Table A-12. Summary of Chemical Sensors and Micrometeorological Techniques used to Measure Deposition Fluxes (adapted from Baldocchi et al., 1988).

Chemical Species	Sensor	Technique <sup>(a)</sup>
$O_3$	Chemiluminescence	EC
	Bubblers	G
NO <sub>2</sub>	Chemiluminescence	EC
	Luminol	EC
$SO_2$	Flame photometry	EC
	UV Absorption	EC
	Bubblers	G
HNO <sub>3</sub>	Nylon filters	G
NH <sub>3</sub>	Absorption traps	G
PM	Optical particle counter	EC

(a) EC: Eddy Correlation Method; G: Gradient Method

sample, as they are usually left open allowing for contamination due to dry deposition. Slightly more sophisticated samplers, and ones which are still in use today, use buckets with automated covers (Eaton and Estes, 1984; Topal and Ozdemir, 1986). An electronic sensor is used to open and close the bucket that is lined with a clean plastic bag. Samples are usually collected on a weekly basis with chemical analysis performed sometime later in the laboratory using standard techniques. More sophisticated samplers can collect samples of shorter duration, that is, multiple samples during a single rain event with storage of the sample at reduced temperatures (Seymour and Stout, 1983; Coscio et al., Kronmiller et al. (1990) describe a sampler that also measures pH and 1982). conductivity in real-time, along with preserving each sample fraction in clean containers maintained at reduced temperatures in a refrigerator, which is part of the sampler. Chemical analysis of the samples can be done in the same manner as with the fog and cloud samples. However, stabilization of labile species would require an operator on the site during sample collection. The deposition can be determined by the amount of water collected, the sampling time, and the size of the collector's inlet.

# Dew, Fog, and Clouds

Determining the deposition of dew and fog to the surface at ground level and interuption of clouds by terrain at higher elevations is typically performed using two approaches. The first approach is to use exposed surfaces such as leaves or a surrogate surface to measure the amount of water collected by that surface over a given time period (Pierson et al., 1988; Collett et al., 1998a). If collected carefully the sample can be analyzed chemically as described above in Section A.2 for the fog measurements. The second approach is to determine the deposition from samples collected using a fog or cloud collector as described above in Section A.2. Accurate determination of fog or cloud deposition by the second approach requires detailed knowledge of the drop size spectra. This can be obtained using, for example, the size fractionating-CASCC and the PMS-CSASP (Collett et al., 1998a) The flux is calculated from the liquid water content, the mass fraction (if size fractionated samples were collected), and the deposition velocity of the droplet. Deposition as a function of drop size is important since the

chemical composition of fog varies as a function of particle size (Collett et al., 1997) and since larger droplets are removed faster than smaller droplets, thus enriching the fog in fine droplet chemical components (Collett et al., 1997; Collett et al., 1998a). Deposition of chemical components to the surface is determined from the measurement of the chemical constituents

## A.7 Measurements of Atmospheric Visibility

Instruments and techniques are available for measurements of various components of atmospheric extinction. Such data are needed to characterize visibility and to provide information for evaluating visibility models and the optical modules of those models. Instruments or techniques that are readily available measure the radiance or luminance, I (and hence the apparent contrast, C); the light extinction coefficient  $b_{ext}$ ; the scattering coefficient  $b_{scat}$ ; and the particle absorption coefficient  $b_{ap}$ . Other instruments that measure a portion of the scattering of light, typically in the backward direction (i.e., back toward a light source) are used for meteorological and aviation purposes, but are poorly suited for air pollution-related visibility assessment and thus will not be discussed here.

Techniques that are in current use for measurement of the air pollution-related optical properties of the atmosphere are described below. The methods discussed here are ones for which there are well-established procedures or commercially available instruments, and that are well suited for routine measurements. Specialized research techniques that require highly skilled operators are not addressed here.

The first several methods discussed below measure properties over a path through the atmosphere, and thus give an average over a path, while the later methods determine properties at a given location. This difference has to be considered when comparing measurement results. In a sense, a long-duration measurement at a point is analogous to a short-duration path measurement along the wind direction, because the long-term sampling integrates over the air mass that the wind carries past the sampling point during the duration of sampling. For example, a one-hour of sampling in a 5 km/h wind integrates over a 5 km long sample, which is analogous to an instantaneous measurement over a 5 km

path. On the other hand, a short-term measurement at a point reflects an instantaneous measurement of a local property.

#### A.7.1 Radiance and Luminance

### <u>Teleradiometers</u> and telephotometers

These instruments, which consist of a telescope and a photocell, measure the amount of light energy arriving from an illuminated object, and thus determine its brightness, I. Teleradiometers measure the radiance, which is the energy at a one or more given wavelengths of light. Telephotometers measure the luminance, which represents the energy integrated over the spectral response of the eye, with the energy at each wavelength weighted with the relative sensitivity of the eye at that wavelength (the photopic response).

Information about the brightness of a scenic element and the horizon sky behind it can be used in Equation (1-1) to deduce the contrast and then in Equation (1-3) to infer  $b_{ext}$  for the wavelength spectrum represented by the measurements, the initial contrast,  $C_0$ , has to be determined by making measurements of the scenic element at a close distance (see Equation 1-3) or on a very clear day (Rayleigh  $b_{ext}$ ) with identical illumination as that at the time of interest (The equations referenced here are in the main body of the report). Accurate determination of the correct  $C_0$  at any instant is difficult in practice, and therefore  $b_{ext}$  determinations by this method tend to have relatively large uncertainty.

Radiance and luminance measurements by teleradiometers, telephotometers, and photography (see below) were in common use in the 1980's to determine apparent contrast and the extinction coefficient. Teleradiometers designed specifically for atmospheric visibility instruments were manufactured by Meteorology Research, Inc. They are no longer manufactured and the company no longer exists. For the purposes of determining atmospheric extinction such instruments have been supplanted by techniques that measure components of extinction directly, rather than the effects of extinction on the appearance of a scenic element. Teleradiometers and telephotometers are still used for visual perception research; such instruments are available from optical instrumentation suppliers.

### **Photography**

Measurement with a densitometer of the densities of scenic elements in a photographic image provides the same information about scenic element radiances or luminances that is provided by the teleradiometer/telephotometer technique. The densitometer determination of information from a spot on the film is analogous to the measurement by a teleradiometer or telephotometer of the brightness of the corresponding spot in an actual scene. Because the response of the film varies with wavelength and the image density not linearly related to the amount of incident light, a photograph of standard color and density charts needs to appear on each roll of film.

The photographic technique (sometimes referred to as sensitometry) requires no complex instrumentation in the field and can be fully automated, and therefore is readily used in remote areas. It has the same technical weaknesses as the teleradiometric/telephotometric approach and is slightly less accurate and precise because of the additional steps of recording an image on film and developing it (Seigneur et al., 1984; Johnson et al., 1985).

Complete camera systems designed for documenting visibility conditions are available from Air Resource Specialists in Ft. Collins, CO. These camera systems are used in many Class I PSD areas in the federal IMPROVE (Interagency Monitoring of Protected Visual Environments) program, although quantitative analysis of the film image is no longer performed. Spot densitometers for measuring the image density are available from several photographic equipment manufacturers. They have been increasingly replaced by film scanners that digitize the entire image for computer analysis.

Digital cameras could be used advantageously for this purpose since the step of digitizing the film would be eliminated, thereby reducing the uncertainty of the measurement. Digital cameras have not yet been applied to atmospheric visibility measurements because reasonably-priced cameras that can provide sufficient resolution are just beginning to appear on the market.

#### A.7.2 Total Extinction

#### Transmissometers

A transmissometer is a teleradiometer that measures the light arriving from an active light source that has been placed at a distance. Typically for the purposes under discussion here, the light source (an incandescent lamp) is located at a distance of several kilometers. Alternatively, the light source can be collocated with the receiver and a retroreflector several kilometers away can be used to produce a path. This instrument measures the attenuation of the light from the source, from which the average light extinction, b<sub>ext</sub>, along the path can be determined from Equation (1-4). Measurements are made instantaneously, although typically several measurements over an hour are used to construct a one-hour average.

As with the need to determine  $C_0$  when using Equation (1-3) for determining extinction, Equation (1-4) requires determining  $I_0$ . This is usually done by placing the source and receiver at a relatively close distance. Because the output of real lamps drifts some with time, errors are introduced in the  $b_{ext}$  determination unless  $I_0$  is measured frequently. This is typically not practical, and so some uncertainty is introduced into typical  $b_{ext}$  determinations.

The transmissometer measures not only the attenuation of light by the aerosol, but also any attenuation of the source brightness due to broadening of the beam by atmospheric turbulence and alteration of the brightness by diffraction. Both of these artifacts will weaken the beam and thus cause the instrument to overestimate the extinction that would be attributed to air pollutants alone.

A transmissometer that is designed for air-pollution related atmospheric extinction measurements is manufactured by Optec, Inc. of Lowell, Michigan. This instrument is used in the federal IMPROVE network.

### A.7.3 Scattering due to Particles and Gases

### **Integrating nephelometer**

An integrating nephelometer determines light scattering by particles and gases,  $b_{scat}$ , by measuring the amount of light that is scattered out of a volume of aerosol over a short (tens of centimeters) path. Nephelometer measurements are continuous, with a temporal resolution of the order of a second to a minute, depending on the design. The instrument is calibrated using particle free air for the Rayleigh scattering point and a halocarbon gas with known scattering for an upscale point.

The geometry of the instrument is such that the optical signal is proportional to the integral of light scattering over (ideally) the full 180° from forward scattering through back scattering (hence the name, integrating nephelometer), and thus it is intended to measure the total light scattered by the aerosol.

In reality, the geometric configuration of real nephelometers does not allow for measurement of scattering in the few degrees around the most forward (0°) and backward (180°) directions (the truncation error). Calibration of the nephelometer using gases compensates for this when the instrument is used to measure light scattering by air, but the correction is incomplete for measurements of particles, which tend to scatter more light in the forward direction than do gases. Nevertheless, the truncation error is quite small (a few percent) for the typically submicron fine particles. The truncation error becomes large for particles larger than a few micrometers, however, and the instrument measures only about half of the scattering from coarse particles of around 10 µm diameter and larger.

Commercially-available integrating nephelometers come in two configurations. One configuration, reflected in instruments from Meteorology Research, Belfort Instruments, Radiance Research, and TSI, measures the air drawn by a fan into a dark, enclosed optical chamber. A different configuration, reflected by instruments from Optec, has an optical chamber that is open on one side to the ambient atmosphere.

The biggest uncertainties of the nephelometric measurements derive from the need to draw the air into an enclosed or partially enclosed sampling chamber. Because of the light source at that chamber, the sampled air is heated slightly, by about 0.5° to 1° C in the

semi-open designs and by several degrees in some of the enclosed configurations. This heating alters the relative humidity of the air and therefore, when the particles being sampled are hygroscopic, dries them out slightly and thus may reduce their scattering. Configurations with sampling ducts also may lose larger particles in the ducts and therefore also underestimate the scattering for this reason.

Consequently, because of sample heating, duct losses, and truncation error, light scattering measurements of ambient aerosol tend to understate the true scattering to some degree.

The drying of particles by the nephelometer can be used to advantage in some situations. By intentionally heating the aerosol enough to dry it below its deliquescence point, the nephelometer will measure only the scattering by dry particles, independent of the ambient humidity (although some hysteresis may limit the amount of water actually evaporating). This makes the instrument readings correlate with dry fine particulate matter concentrations and to be independent of weather. The correlation can be further enhanced if the inlet to the nephelometer contains a cyclone that excludes the larger particles that are poorly measured by the instrument; the cyclone can also be used to exclude fog droplets. This approach only works for nephelometers with fully enclosed sample chambers, however. In such modified forms the integrating nephelometer is less a visibility instrument and more an aerosol characterization instrument.

Integrating nephelometers in two designs were manufactured from 1969 to about 1982 by Meteorology Research, Inc. (MRI). The manufacture of one design was continued for some years afterward by Belfort Instruments. Many of the MRI/Belfort instruments are still in use. Currently, instruments are available from Optec, Inc. of Lowell, Michigan, and TSI Inc. of St. Paul, Minnesota. Also, Radiance Research of Seattle, Washington, has produced an updated version of the MRI/Belfort instruments. The Optec instruments, which are optimized for long-term, unattended operation outdoors, are used in the federal IMPROVE network. The TSI instruments are designed for research settings.

## A.7.4 Absorption due to Particles

# Integrating plate

Light absorption due to particles,  $b_{ap}$ , can be determined by collecting particulate matter on a filter and then measuring the transmittance of light through the filter in the laboratory, generally many days after sample collection. These measurements are typically made on multi-hour filter samples. The technique is called the integrating plate method because of an element in the optical system that integrates the light that passes through the sample.

Standard particulate matter samplers are used for collecting the samples. Typically, only the fine fraction (aerodynamic diameter smaller than 2.5 µm) is collected through use of a size-selective sampler inlet. The laboratory equipment for the absorption measurements is specially configured by each laboratory. Two facilities that make such absorption measurements include the University of California at Davis (UCD) and the Desert Research Institute (DRI) in Reno, Nevada. UCD is making the absorption measurements for the federal IMPROVE network. The absorption determinations by the two laboratories don't always agree and there is a current debate about the correct way to make such measurements. Research techniques for determining absorption, such as photo-acoustic measurements, are being used to help resolve the discrepancy.

#### <u>Aethalometer</u>

The integrating plate light absorption method is automated in the field by an aethalometer. The aethalometer collects particles onto a spot on a filter tape and determines light absorption by measuring the attenuation of a light beam passing through the tape and the material on the filter. Measurements have a temporal resolution of a few minutes to an hour, depending on the amount of absorbing material in the air. The tape is periodically advanced to a new spot after the particulate loading has become sufficiently great to significantly reduce the transmittance.

The aethalometer is available commercially from Magee Scientific. Its measurements have been found to agree on average with filter/integrating plate

determinations by DRI, albeit with considerable point-to-point scatter (Tombach et al., 1996).

### A.7.5 Absorption due to Gases

Light absorption by gases in the troposphere is due primarily to NO<sub>2</sub>. Light is absorbed by NO<sub>2</sub> primarily in the violet-blue range (i.e., from about 400 to 450 nm) and an atmosphere with high NO<sub>2</sub> concentrations appears brown to the human eye, since most of the blue light has been removed. Measurement of light absorption by NO<sub>2</sub> has been conducted for NO<sub>2</sub>-ladden plumes using teleradiomety or sensitomety (See section A.7.1). For regional haze, however, light absorption by NO<sub>2</sub> is typically estimated from measurements of NO<sub>2</sub> concentrations combined with the absorption characteristics of NO<sub>2</sub> (Dixon, 1940). Measurements of NO<sub>2</sub> concentrations are described in Section A.1.

# A.7.6 Summary of Instrument Performance

Table A-13 summarizes key aspects of the performance of the methods described above, when operating under field conditions. Quantification of instrument uncertainties is difficult, appropriate standards do not exist, and therefore the evaluations that have been done tend to be limited. Furthermore, instrument performance in laboratory tests tends to differ from that in the field. In many cases, expert judgment is the only guide to assessing performance. Consequently the information in Table A-13 is incomplete and the data that are there should be viewed as a qualitative guideline to instrument performance for carefully-operated instruments.

Since the sum of the integrating nephelometer and aethalometer measurements should equal the transmissometer measurements, it is possible to make measurements with an internal consistency check. But, because of the different spatial scales of the measurements and the different responses of the instruments to moisture in the atmosphere, this check does not always show full agreement. In particular, the propensity of the integrating nephelometer to underestimate the scattering must be taken into account.

Table A-13. Summary of Performance of Visibility Measurement Techniques

Method	Variable Measured	Limit of Detection	Precision	Accuracy	Potential Interferences/ Artifacts	Comments	References
Teleradiometer or telephotometer	I used to infer C and b <sub>ext</sub>		C = 0.02 (MRI instrument)	C = 0.01 (MRI instrument)	Non-standard illumination (clouds)	$b_{ext}$ determination very sensitive to $C_0$	Bergstrom et al., 1982
Integrating nephelometer	b <sub>scat</sub>	1 Mm <sup>-1</sup>	2 - 5 Mm <sup>-1</sup>	~2 Mm <sup>-1</sup> for fine particles at low RH	Sample heating, sample loss, truncation error	Different makes have differing characteristics	Tombach & Thurston, 1995; Molenar, 1997; Day et al., 1997
Integrating plate analysis of filter sample	$b_{\mathrm{ap}}$				Optical interference between filter and particles and shadowing of one particle by another	Disagreement as to correct way to correct for artifacts; all uncertainties depend on sampling duration	Lin et al. , 1973
Aethalometer	b <sub>ap</sub>		~1% (theoretical), 10% in practice	<1 Mm <sup>-1</sup> (theoretical)		All uncertainties depend on sampling duration	Watson et al., 1996, App. A; Tombach et al., 1996
Transmissometer	b <sub>ext</sub>	~1 Mm <sup>-1</sup>	~2 Mm <sup>-1</sup>	~1 Mm <sup>-1</sup>	Atmospheric turbulence and refraction; fog	Accuracy affected by lamp brightness drift	Malm & Persha, 1991

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It should also be noted that all of these techniques are appropriate when the visibility effects of PM-2.5 are of interest. To the extent that visibility impairment also results from larger particles, the transmissometer is the only device that can reflect that large-particle extinction correctly.

#### A.7.7 Recommendations

The light extinction, scattering, and absorption measurements can be used separately to evaluate the performance of particular portions of visibility models (see Section 2.4).

Because of the effect of humidity on the scattering of light by particles, light extinction, scattering, and absorption data can be used in two ways in visibility analyses and modeling:

- The "ambient" method: Here all measurements are made so as to represent ambient conditions as well as possible. Because most nephelometric light scattering measurements begin to show errors above RH = 70%, their usefulness becomes limited. Above RH = 90%, all nephelometer measurements become unreliable and transmissometer measurements are influenced by clouds or fog. Furthermore, at those high humidities it is difficult to measure the RH itself accurately, which makes use of aerosol thermodynamic models less reliable. Therefore, typically, data taken above an RH of 90% are not used for air pollution aerosol optics analyses.
- The "dried" method: In this approach, the ambient aerosol is dried by passing it through a desiccator or heater, and then its scattering is measured by an integrating nephelometer. The light absorption measurements are not affected by moisture, and thus do not require the pre-treatment. These dried aerosol optical measurements can then be used for evaluating the performance of an aerosol and visibility model without need for estimating

the contribution of water to light scattering. The transmissometer can not be used in this approach because there is no way to dry the aerosol it observes.

As a variant of the second method, integrating nephelometers have been used to measure the interstitial aerosol in the presence of fog (Watson *et al.*, 1996). To accomplish this requires an enclosed nephelometer with a cyclone (typically with a 2.5 µm cut point) at the inlet. The cyclone removes fog droplets and leaves the fine particles. Of course, any effect of sample heating is reflected in the subsequent measurement of scattering unless the sample is then intentionally heated to observe the dry particles.

# Ground-Based Measurements

The most commonly used configuration for ground based measurements consists of a transmissometer for  $b_{ext}$ , an integrating nephelometer for  $b_{scat}$ , and either an aethalometer or filter sampler for  $b_{ap}$ . This configuration provides some redundancy in measurements, as described above.

Since the transmissometer is the most expensive of these instruments to purchase, install, and operate, and also requires a several-kilometer sight path, it is often left out. The nephelometer and aethalometer pair can provide a good characterization of the aerosol with relatively short time resolution if the propensity of the nephelometer to underestimate scattering is taken into account.

### Measurements Aloft

The only instrument described above that has been used successfully in aircraft is the integrating nephelometer of the enclosed type. Because of its fast response it has served often to characterize the spatial distribution of aerosol in aircraft surveys.

Filter sampling can be used to collect samples for b<sub>ap</sub> analysis, but the low flow rates characteristic of aircraft filter samplers and the low particulate matter concentrations aloft dictate long sampling times (typically over 1/2 hour) to get sufficient sample for

analysis. Such samples can be used to describe conditions aloft, but they do not provide high-resolution information on spatial distribution (see Section A.8).

## A.8 Sampling from Airborne Platforms

Chemical and meteorological measurements aloft are essential for understanding atmospheric dynamics, chemistry, and transport. Upper air meteorological measurements are now routinely conducted in intensive field measurement programs using remote sensing from surface based instruments, such as radar wind profilers, doppler acoustic sounders, or balloons launched from the surface and tracked either optically or by radio. These upper air meteorological measurements are described in Section A.4. This section addresses gas- and particulate-phase measurements from aloft sampling platforms.

There are basically five platforms that can be used to measure chemical components aloft. These include the use of tethered balloons, free balloons (or sondes), tall towers (typical maximum height is 615 m, e.g., the Boulder tower), aircraft, and satellites. Each of these platforms provides different options for measurement programs, and their use depends on study objectives, cost, and species of interest. balloons and towers typically represent point measurements at some height above the surface; although both can provide some vertical resolution if multiple systems are used at different heights. However, spatial resolution is limited to one point per system. Towers also are limited in height (maximum radio tower heights are in the range of 400 m, see for example the tower used in IMS95, Collett et al., 1997) and in location, as there are few tall radio towers available in a given area. Building a temporary tower is an option; it is however expensive and limited in vertical height (e.g., \$100,000 for a 100 m tower installed for one year; Neff, NOAA, personal communication, 1998). Towers and tethered balloons allow for sampling at one height for extended time periods, thus allowing the boundary layer to move back and forth across the sampling location if placed correctly. Samples collected by free balloons, on the other hand, provide considerable vertical resolution and extended heights, but sample a given point in space only once. Satellites have been used widely for stratospheric measurements, but even there often lack the sensitivity needed for small scale resolution, in both the vertical and

horizontal dimensions, as well as analytical sensitivity (Brune and Stimpfle, 1993). Aircraft, while expensive to operate for long-term programs, have many advantages over these other platforms in regional field programs, and to date, aircraft are the most widely used platforms for chemical measurements aloft.

Requirements for sampling aloft aboard a moving aircraft platform are different and typically more stringent than those for monitoring at a point location at the surface. Nevertheless, measurement methods have been developed or modified to meet many of these requirements. Some specific examples are provided in Daum and Springston (1993) for the measurement of O<sub>3</sub>, SO<sub>2</sub>, NO<sub>x</sub>, CO, H<sub>2</sub>O<sub>2</sub>, PM, and cloud water liquid water content. Parrish and Fehsenfeld (1998) also describe examples of methods used aboard aircraft and specifically present brief summaries of methods intercomparisons that have occurred aboard aircraft platforms. As with surface measurements, some of these pollutants require the collection of time-integrated samples with subsequent chemical analysis in the laboratory or even aboard the aircraft, while other methods are continuous. Time-integrated methods include the use of filter packs to collect PM and precursor gases where the collected PM can be analyzed for chemical constituents at a later time, the collection of cloud water or precipitation using methods similar to the fog and cloud collectors described in A.3, and the collection of grab samples using canisters, cartridges, or inert sampling bags (e.g., Tedlar bags). Continuous methods include chemically based analyzers, such as chemiluminescence methods for ozone and NO<sub>x</sub>, or spectroscopic methods.

Special measurement challenges encountered when using aircraft measurement platforms include 1) engineering design considerations, such as size, weight, and electrical consumption of the instrument, all of which must be minimized for sampling aboard aircraft platforms, and robustness to handle the excessive electrical and vibrational noise associated with the aircraft; 2) measurement considerations, such as the analytical sensitivity of the method, time resolution needed to meet study objectives, and effects of rapid changes in temperature, pressure, and relative humidity; and 3) aircraft design considerations, which pose special challenges, such as those associated with design and location of sample inlets and manifolds. Daum and Springston (1993) recently reviewed sampling considerations associated with the use of aircraft platforms

for obtaining gas- and particulate-phase measurements aloft, while McMurry (1998) highlighted considerations associated with sampling inlets and collection of particles and gases at high speeds. The discussion below summarizes important points from these reviews.

Sampling from a platform that can change altitude quickly requires either methods that are independent of changes in temperature, relative humidity, and pressure, or a methodology to correct for the effect of changes on these variables on the data collected. The largest concern comes from changes in pressure that result from changes in altitude. Sensors can be mass dependent or concentration dependent. True mass dependent sensors are independent of pressure, while concentration dependent sensors are dependent on pressure. However, it may not be obvious for the sampling-detection system as a whole, since one component of a system may be mass dependent, while another may be concentration dependent. An example of this situation is given by Daum and Springston (1993), who point out that the measurement of SO<sub>2</sub> by the flame photometric instrument has both mass and concentration dependent components.

Instrument response time is another critical factor when sampling aboard aircraft platforms. For example, aircraft used to collect pollutant data in the lower troposphere typically fly at speeds from 50 to 200 km/s. Therefore, a 10 s sample covers a spatial extent from 0.5 to 2 km, while for a one-hour sample the distance covered would range from 180-720 km. A one-hour averaged sample results in a spatial distance much greater than the grid size currently in use in Eulerian air quality models. Therefore, short integration times are desirable. There is however a trade-off between resolution, sensitivity, and noise. Shorter sampling times often result in more noise, poorer precision, and less sensitivity.

The sample inlet or probe and transfer tubes must be designed so that the composition of the ambient sample is not altered, chemically or physically. Sampling from a moving platform creates a particularly difficult challenge for the collection of particles, if the size distribution and phase equilibrium must be preserved. The size distribution can be altered if sampling is not conducted under isokinetic conditions, resulting in either positive or negative biases. Phase equilibrium can change due to compression heating of the gases as they are slowed and undergo adiabatic compression

in the collection tube. Both potential problems can be minimized by careful design of the sampling system. In general, collection of gases require the same considerations as sampling at ground level, with most concerns centered around the loss of reactive species on sampling inlets and transfer tubes. However, with aircraft, special consideration must be given to the condensation of water on transfer tubes, that may result in the potential for additional losses of gas-phase species. The sampling probe must extend outside the boundary layer of the aircraft and be free of the propeller-wash and pollutant emissions from engine exhaust and engine heaters.

When sampling from an aircraft, consideration must also be given to the payload and power capabilities of the aircraft. A small plane may be able to carry payloads only as large as 250 kg with very limited space available. Consequently, many ground-based methods have been modified to be smaller and lighter in weight. Aircraft also typically operate on 28 v DC and 400 Hz, while laboratory methods typically operate at 110 v or 220 v and 60 Hz. Therefore, special converters must be added to the aircraft or the instruments must be converted to 28 v.

## Section 8. Regulatory Changes and Schedule

#### 8.1 Introduction

There are three main Federal regulations that are used to provide the framework for ambient air quality monitoring, 40 CFR parts 50, 53, and 58. These regulations cover the sampling and analytical methods used, how new methods are approved, quality assurance and control procedures, and basic monitoring objectives for certain air pollutants. The focus in this section is the air monitoring regulations and how they will be revised to support the national ambient air monitoring strategy (Strategy).

EPA is reviewing and intends to modify appropriate regulations to incorporate more continuous particle techniques, to revise the national air monitoring requirements for each criteria pollutant and ozone precursors, and to update the data reporting requirements to reflect the development of newer databases and electronic storage capabilities. EPA will provide ample flexibility for State, local, and tribal (SLT) agencies to address their regional or local concerns.

EPA is considering including the regulatory changes necessary for the monitoring strategy into the regulatory changes needed for the ongoing PM NAAQS review. The PM NAAQS review may result in EPA establishing a new coarse particle NAAQS and its associated air monitoring requirements. There is significant overlap between these two activities.

## 8.2 Specific Regulations to be Reviewed

There are three main regulatory "Parts" of the Code of Federal Regulations (CFR) that will be investigated to modify the monitoring regulations. These regulations are all part of CFR Title 40 which deals with the environment. Specifically:

1. 40 CFR 50, Appendices: National Primary and Secondary Ambient Air Quality Standards (NAAQS), Appendix L. This regulation provides for the NAAQS and the Federal Reference Methods (FRM) for measuring each air pollutant with an established standard. There is an ongoing PM NAAQS review that is very likely to result in establishing a PMcoarse (PM<sub>10</sub>-PM<sub>2.5</sub>) NAAQS. Accordingly, there will be a need to include a FRM for PMcoarse into the regulatory changes if this decision is made. The EPA's Office of Air Quality Planning and Standards is working with the Office of Research and Development (ORD) laboratory that will provide for this new PMcoarse method. The current thinking is that a sequential dichotomous sampler may be selected as the PMcoarse FRM. If this method is selected, it would need to be developed as a useful federal equivalent method (FEM) for PM<sub>2.5</sub> and PM<sub>10</sub> as well.

EPA will review the existing  $PM_{2.5}$  FRM to identify areas where burden can be reduced or eliminated. This will include a review of the Appendix L text which describes the reference method for measuring  $PM_{2.5}$ , and a variety of sampler operational parameters that must currently be reported. EPA has sufficient information at this time to understand the  $PM_{2.5}$  FRM operation, and could possibly reduce the number of parameters that monitoring agencies must report as supplementary data. EPA does not expect to change the overall  $PM_{2.5}$  FRM.

- 2. 40 CFR 53 Ambient Air Monitoring Reference and Equivalent Methods. This regulation provides air quality monitoring instrument manufacturers with the application and testing requirements for reference and equivalent methods that must be followed in order to have their sampler/analyzer approved for regulatory use. EPA/ORD is currently responsible for these approvals. EPA will review this regulation and identify where changes may be possible to allow for more options in PM FEMs.
- 3. 40 CFR 58 Ambient Air Quality Surveillance. Nearly all data collection and reporting requirements, all the quality assurance requirements, the NAAQS pollutant network design criteria, the air quality index reporting, and annual data certification requirements are included within this regulation. Part 58 describes how the Clean Air Act air monitoring authority has been interpreted and implemented by the EPA and our State and local agency partners for air pollutants with established NAAQS. Tribal agencies are not regulated under this provision; however, the technical requirements within should be familiar to any tribal agency that plans to conduct monitoring. At this time, EPA expects to include the following items in this regulatory package:
  - adopt NCore as a replacement for the NAMS/SLAMS network requirements;
  - continue to provide monitoring requirements for areas that violate or are suspected of violating a NAAQS (any pollutant), and reduce requirements in areas that have established their attainment status;
  - adopt a regulatory structure for ozone and PM<sub>2.5</sub> that includes consideration for historical concentration values in addition to population. (Current requirements are based largely on population figures of cities);
  - continue to support the need for air monitoring agencies to customize their network to address their local data needs;

- reduce data reporting where possible, and update existing data reporting requirements to push for more automated data processing and management systems;
- promote air quality reporting to the public with emphasis on being able to map air quality and promote the Air Quality Index;
- revise the two quality assurance appendices to reflect current program needs. Define a graded approach for quality assurance activities; more specifically, tailoring the quality system and quality assurance project plan development to the data collection objectives; and
- simplify the language of the whole regulation.

## **8.3** Participants in the Regulatory Review

EPA has engaged a variety of parties for this regulatory review process. The NMSC is providing broad recommendations for the national air monitoring program that will require regulatory changes. Their recommendations include a multi-level NCore approach that emphasizes measuring multiple air pollutants at key locations and additional air monitoring to promote ozone and PM mapping and public data reporting. To manage this work, three separate work groups were created, one each for the subjects of regulatory review, quality assurance, and technology.

The quality assurance group is providing recommendations for changes to the quality assurance provisions of the monitoring regulations as well as all existing quality assurance practices. (See Section 5.) The technology work group is making recommendations for use in the methods sections of the regulations and in technical guidance used by monitoring agencies. (See Section 6.) The regulatory review work group must take the information from all of these parties, in addition to the NMSC, and review the 40 CFR 58 requirements to develop an appropriate regulatory package.

The NMSC and the three work groups include representatives from the EPA OAQPS, the ten EPA Regional Offices, State agencies, local agencies, and tribal governments. In moving forward, all regulatory changes will undergo public review and comment inherent within the regulatory modification process. EPA will also work through existing mechanisms such as the STAPPA/ALAPCO Monitoring Committee and the Standing Air Monitoring Work Group (SAMWG) to communicate with stakeholders on these regulatory changes.

#### 8.4 Schedule

These schedules are best estimates for when this work will be complete.

- October 23-25, 2001 Monitoring Strategy Workshop (kickoff regulatory review)
- · January-July 2002 NMSC finalizes their recommendations.
- · October 2001 December 2002 Regulatory review work group to develop ideas for regulatory modifications. Regulatory sections are drafted.
- December 2002-February 2003 EPA prepares cost estimates, reviews regulatory change, obtains agreement within office on content.
- sJune 2003- Proposal in the Federal Register (approximate date).
- · 90-day Public comment period.
- December 2003 Final regulatory package published in Federal Register (approximate date).

EPA did consider merging the regulatory packages on the Monitoring Strategy and the regulatory package for the PM NAAQS review. The current difference in schedules between the Monitoring Strategy and the PM NAAQS review is significant, and would delay making progress in realizing many of the Monitoring Strategy goals. These package will not be combined at this time. EPA may have to address certain PM monitoring issues, such as certain uses of continuous PM samplers and modifications to the FRM/FEM criteria, within the PM NAAQS package.

## Section 9. Communications and Outreach

#### 9.1 Introduction

The development of the Monitoring Strategy and the move toward implementation require an important set communication tools to make sure State and local agencies, tribes, public interest groups, the business sector, and the general public have access to information on a timely basis. Without a concerted communications and outreach effort, expected changes to air monitoring networks may not be understood and appreciated for their benefits, which are summarized below. A more specific communications strategy, plan, and products will be developed and implemented by EPA with collaboration from STAPPA/ALAPCO, NMSC and Tribes.

# 9.1.1 Benefits to State and Local Air Agencies, Public Interest Groups and the General Public

- Increased data to the public: The Strategy seeks to incorporate new, continuous
  technologies into the national network. Incorporation of these new technologies
  will lead to more efficient, electronic reporting of real-time data (similar to the
  ozone network reporting system). Moving from filter-based methods and
  periodic reporting, to continuous methods and subsequent satellite-GIS type
  reporting via internet networks will provide the public with more timely and
  current information.
- Conservation of Resources. Periodic review, assessment, and realignment of the
  monitoring network assure that resources are prudently invested to meet the most
  pressing air monitoring needs. This does not mean omitting monitors in crucial
  areas: it simply means using the local regional assessment to determine which
  monitors are providing redundant or little-value-added information and relocating
  them to locations which will provide more meaningful data.
- Integrated NCore Monitoring. Since NCore sites will include multiple-pollutant measurements, the foundation for health studies is improved, and future information about pollutant health effects will benefit the public. Also, a local area will have a basis for comparing its local measurements with national data, since each NCore Level 2 site will include similar monitors, FRM methods, and laboratory techniques. Trend assessments will also be performed at the NCore sites, which will yield more valuable information about the local area's air quality in relation to the Nation.
- More Resources for Local Issues. As NCore is implemented, there will be greater
  emphasis on monitoring programs to meet local needs. This flexibility, created
  by splitting Federal funds between Level 2-3 NCore sites and local sites, will
  allow agencies to monitor for pollutants which are of greatest importance to local
  communities. These needs could cover hot-spot monitoring, local source

characterization, environmental justice issues, or any other need the local authority deems necessary.

Public Involvement. A public education and outreach program is needed to communicate the purposes of air monitoring networks and to ensure adequate public involvement early in the process. State, local and tribal agencies are encouraged to identify special interest groups and conduct outreach efforts as appropriate to discuss potential monitoring network changes, with the understanding that monitors are placed to meet specific objectives, both national and local. Once those objectives are met, site and monitor relocations are a necessary process to assure that new objectives and priorities will be met in the best way possible. The public needs to be aware that consolidation or relocation of a monitor or monitoring station within a community means an improvement in the quality, value, and timeliness of the information provided by the network. SLTs are working with EPA to develop such a public education and outreach program.

# 9.1.2 Benefits to the Research and Academic Community

The networks operated by State and local agencies provide an enormous resource of "routine" data that complement the more advanced measurements conducted by research organizations. The data help them attempt to uncover the specific causes of adverse health effects related to air pollution, or test air quality simulation models that try to replicate the complex physical and chemical behavior of the atmosphere.

The NCore network will be designed to ensure that long-term research interests will benefit from the routine monitoring conducted by SLTs. This strategy recognizes the leveraging value of a spectrum of other air monitoring efforts, including intensive research oriented studies (NARSTO, PM<sub>2.5</sub> Supersites, CRPAQS, PM health centers), deposition monitoring (CASTNET, IADN, NADP) and numerous other smaller research projects. NCore will also provide, via the Level 1 "supersites," several national locations convenient for testing newly developed monitoring instruments under differing meteorological and air pollutant regimes.

It is anticipated that the NCore approach will meet scientific air monitoring needs to a much greater degree than the networks currently provide.

#### **9.1.3** Benefits to Tribal Communities

The Strategy will have many of the same benefits for tribal air programs as it does for State and local agencies. However, the benefits of additional flexibility in targeting monitoring to each reservation's needs and priorities will be particularly important for the tribes. This flexibility is particularly important because the tribes are in the process of assessing air quality on Indian lands, and thus have ability to explore environmental and health concerns that are specific to their needs.

There is an additional resource benefit for the tribes as well. Because the tribes are in the initial stages of monitoring, air program development and resources for conducting monitoring on Indian lands are extremely limited. Monitoring equipment released from the network from other areas may be available for tribes at little or no cost. Given that there is very limited existing air monitoring on Indian lands, such instruments might provide air quality information that otherwise might not be available. But not all reservations or Indian communities will need or want to conduct monitoring. In these areas, the Strategy can provide information on local and national air quality that can help tribes and community members track air quality trends in their area.

It is expected that tribal participation in the Strategy will enhance the value of NCore by meeting specific Strategy objectives that might not be fully met by state and local agencies alone, such as rural siting, urban-rural couplets, or possibly transport or background needs. While it is envisioned that most tribal air monitoring will be at the Level 3 or local level, those tribes that have the expertise and resources to establish a Level 2 site will be able to help meet these specific objectives.

#### 9.2 How This Information Will be Communicated

The essential information contained in the preceding paragraphs need to be communicated effectively to several different audiences. To do this, several communication products are currently being planned and/or developed:

- (1) Fact Sheet. At approximately the same time as the release of the Draft Strategy Document, a fact sheet will be posted on AMTIC and distributed to SLTs explaining, in general terms, the technical need for a revised air monitoring strategy. This fact sheet is approximately two pages in length, and covers points on continuous monitoring technology as well as establishment of an "NCore" network. This item will target most audiences.
- (2) Quarterly Newsletter. Beginning August 2002, a quarterly newsletter is being distributed on AMTIC. (The website address is:

## http://www.epa.gov/ttn/amtic/newsltr.html

The newsletter provides updates on reviews, availability of materials (documents and presentations), the regional assessments, and other timely topics. The target audience is agency, tribal, and all public/private representatives with a more detailed interest in the latest progress for the Strategy.

(3) <u>Specialized Briefing Presentations</u>. Several packaged slide presentations are being developed for use and dissemination to different audiences. One will be more technical and detailed and will be targeted for use by EPA

Regional representatives, and SLTs (regional briefing package). A second presentation will be tailored for public interest groups, and knowledgeable groups and individuals (public interest briefing package). A third presentation will be simpler and less technical, and can be used by federal, state and local agencies and tribes in communicating the Strategy to the general public (public-oriented briefing package). Having these packages available will help to assure consistency in communications throughout the country.

(4) Monitoring Strategy Brochure. A trifold (or similar) brochure will be developed for a simplified, concise, non-technical explanation of the Strategy and air monitoring networks in general. This brochure will be developed by EPA, and coordinated with STAPPA/ALAPCO, for distribution shortly after the finalization of the Strategy Document in early 2003. The brochure is targeted primarily for the general public.

# **9.3 Preliminary Schedule**

In developing a communications strategy, the following preliminary schedule has been developed:

August 2002 – December 2003: Quarterly Newsletter posted on AMTIC

September 2002: Release of Fact Sheet

Communications plan developed

Fall 2002: Availability of regional and public interest briefing packages

Winter 2003: Release of Final Strategy Document

Press release issued by EPA

Brochure completed for distribution to the public Availability of local, public-oriented briefing package

### 9.4 Review and Feedback

Proceeding forward with the finalization of the Strategy will require important feedback from the scientific community, state and local air agencies, tribes, interested environmental and industry/business groups, and the general public. The NMSC has put forth its best effort in constructing the framework for the Strategy, but it is extremely important for the NMSC to receive constructive commentary. To that end, two approaches are being taken:

(1) Scientific Review and Feedback. A subcommittee of the Clean Air Scientific Advisory Committee (CASAC) is expected to be convened in the Fall of 2002.

This committee will review the Strategy and provide comments on its scientific merit. Also, interactions with other scientific groups have already occurred, including the Air Quality Research subcommittee of the Committee for Environment and Natural Resources (CENR), the NARSTO Executive Assembly, and the PM Supersite Principal Investigators. It should be noted, too, that a representative from EPA-ORD is a member of the NMSC, providing scientific guidance and perspective to the NMSC during its development of the draft Strategy.

(2) Agency/Tribe/Stakeholder/Public Feedback. Through the release of this document and the companion Summary Document, all interested persons are invited to review and comment on the Strategy. Comments are due by Friday, November 22, 2002, and should be sent to:

Ms Brenda Millar or e-mail:

U.S Environmental Protection Agency <u>millar.brenda@epamail.epa.gov</u>

*OAQPS, C339-02 or fax:* 

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The NMSC will review comments prior to finalizing the National Air Monitoring Strategy Document, likely in early 2003.